

# Chapter 8

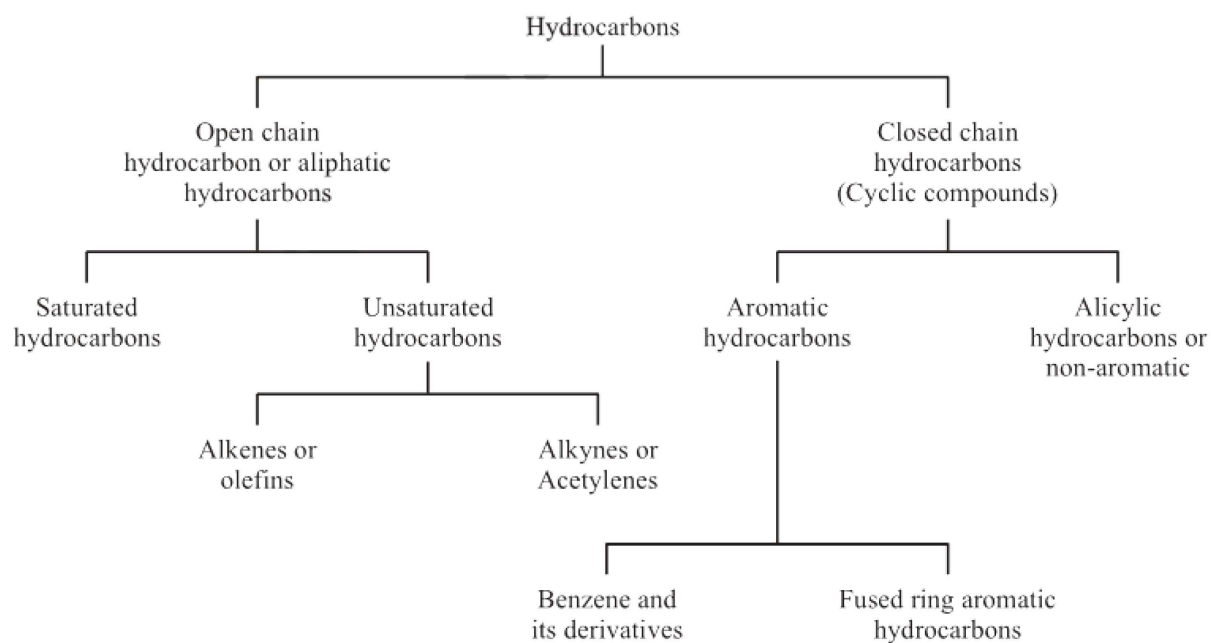
## ALIPHATIC HYDROCARBONS

The organic compounds which contain carbon atoms and hydrogen atoms only in them are called hydrocarbons. e.g.,



Hydrocarbon compounds are in large numbers and divided into various classes. Hydrocarbons are classified on the basis of structure of chain, size of chain and nature of the rings.

### CLASSIFICATION OF HYDROCARBONS

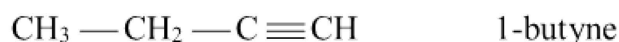
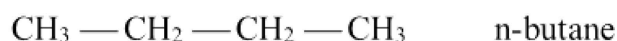


Hydrocarbons are classified into two major classes:

- (1) Open chain hydrocarbons (aliphatic hydrocarbons)
- (2) Closed chain hydrocarbons (cyclic)

### (1) Open Chain Compounds:

The hydrocarbons in which both ends of carbon chain are open, are called open chain compounds. e.g.,

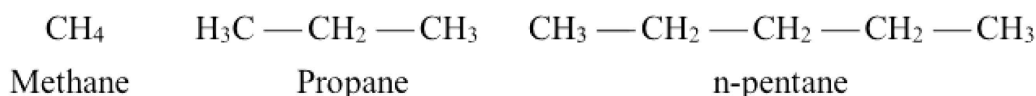


These hydrocarbons are of mainly two types:

- (a) Saturated hydrocarbons
- (b) Unsaturated hydrocarbons

#### (a) Saturated Hydrocarbons:

*“These are the compounds of carbon and hydrogen in which the valency of carbon is fully saturated and there is single bonds between carbon and carbon atoms.”* Their general formula is  $\text{C}_n\text{H}_{2n+2}$ . e.g.,



Due to their least chemical reactivity, the saturated hydrocarbons are also known as ‘Paraffins’. The name ‘Paraffins’ comes from the combination of Latin word “parum” and “affin”.

Parum = Little,

Affin = Affinity

#### (b) Unsaturated Hydrocarbons:

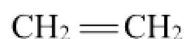
*“Compounds of carbon and hydrogen, in which the valency of carbon is not fully saturated, are called unsaturated hydrocarbon.”*

Unsaturated hydrocarbons are grouped into two categories:

- (i) Alkenes or Olefins
- (ii) Alkynes or Acetylenes

#### (i) Alkenes or Olefins:

Those hydrocarbons in which there is a double bond between carbon and carbon atoms are called alkenes or olefins. Their general formula is  $\text{C}_n\text{H}_{2n}$ . e.g.,



Ethene



Propene



**(ii) Alkynes or Acetylenes:**

*“Those hydrocarbons in which there is a triple bond between carbon and carbon atoms are called alkynes or acetylenes.”* Their general formula is  $C_nH_{2n-2}$ . e.g.,



(Ethyne) Acetylene



Propyne

**(2) Closed Chain Hydrocarbons:**

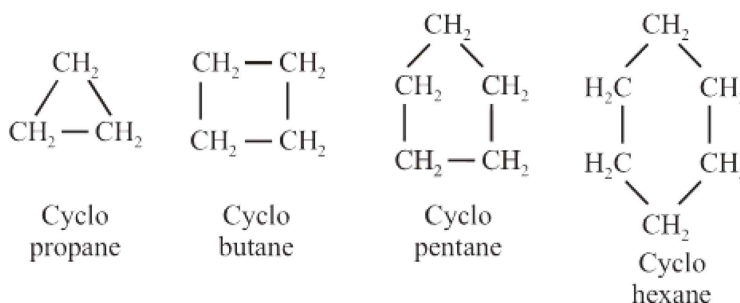
*“Closed chain hydrocarbons are the compounds of carbon and hydrogen which contain rings of carbon atoms.”*

These are of two types of closed chain compounds:

- (a) Alicyclic hydrocarbons
- (b) Aromatic hydrocarbons

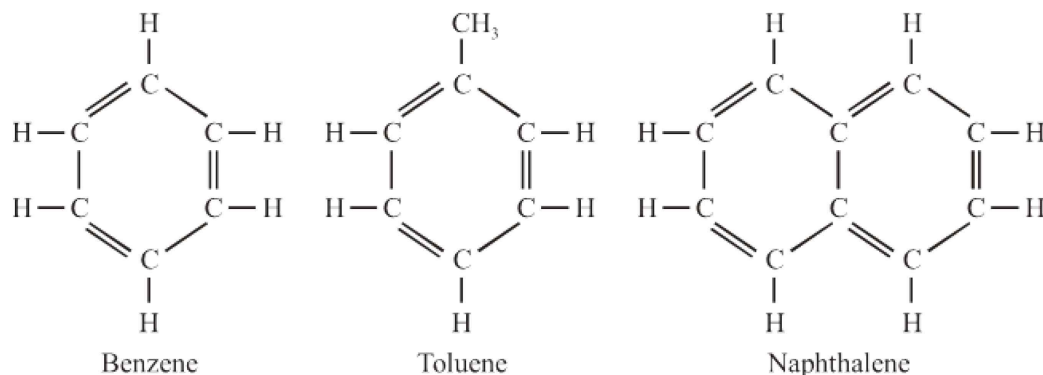
**(a) Alicyclic Hydrocarbons:**

*“Cyclic hydrocarbons that do not contain a benzene ring in them are called alicyclic hydrocarbons.”* e.g.,

**(b) Aromatic Hydrocarbons:**

*“Cyclic hydrocarbons are those which contain a benzene ring in them, are called aromatic hydrocarbons.”*

A six-member ring of carbon atoms with alternating single and double carbon-carbon bonds is called a benzene ring. e.g.,

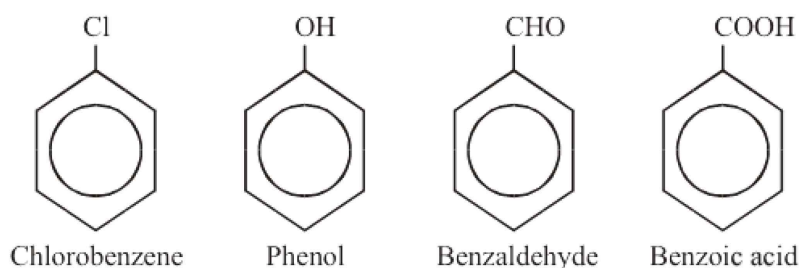


Aromatic compounds are further classified as:

- (i) Benzene and its derivative
- (ii) Fused ring aromatic compounds

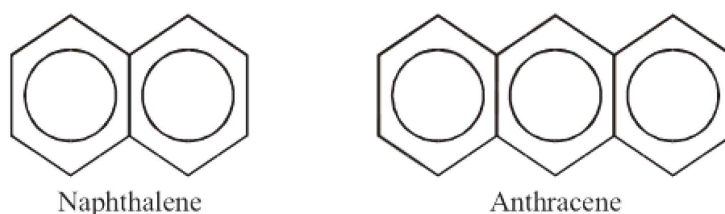
**(i) Benzene Ring Derivatives:**

*“The compounds in which one or more hydrogen atoms of benzene ring are replaced by any functional group or alkyl group are called benzene derivatives.” e.g.,*



**(ii) Fused Ring Aromatic Compounds:**

*“The hydrocarbons which have two or more aromatic rings, fused together, called fused ring aromatic compounds.” e.g.,*



<b>NOMENCLATURE</b>
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**Common or Trivial Names:**

In the early days, the compounds were named on the basis of their history; the method of preparation or name of the person working on it, e.g., the name **marsh gas** as given to methane because it was found in marshy places. Acetic acid derives its name from vinegar (Latin, acetum means vinegar). Organic compounds were named after a person (Barbara) like barbituric acid ( $C_4H_4N_2O_3$ ). Such a system may have a certain charm but is never manageable.

In this system, first four members of the series are known as methane ( $CH_4$ ), ethane, ( $C_2H_6$ ), propane ( $C_3H_8$ ) and butane ( $C_4H_{10}$ ). Rest of the members are named by prefixing Greek numeral, indicating the number of carbon atoms (penta, hexa, hepta, etc.) and the suffix “ane”.

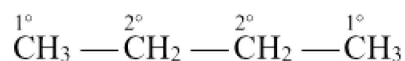
**TYPES OF CARBON ATOMS IN SATURATED HYDROCARBONS**

Usually in saturated hydrocarbons, four types of carbon atoms are present:

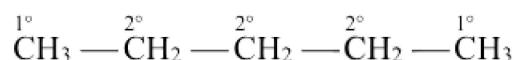
- (1) **Primary ( $1^\circ$ ) carbon:** Atom having either one or more of its valencies satisfied with another carbon atom.
- (2) **Secondary ( $2^\circ$ ) carbon:** Atom having its two valencies satisfied with two other carbon atoms.
- (3) **Tertiary ( $3^\circ$ ) carbon:** Atom having its three valencies satisfied with three other carbon atoms.
- (4) **Quaternary ( $4^\circ$ ) carbon:** Atom having its all the four valencies satisfied with four carbon atoms.

Some points for common naming are given below:

- (i) In open chain hydrocarbons only primary and secondary carbon atoms are present. e.g.,



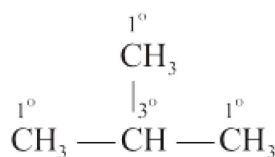
(n-Butane)



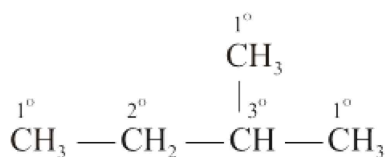
(n-Pentane)

Such carbons are termed as normal and denoted by “n”.

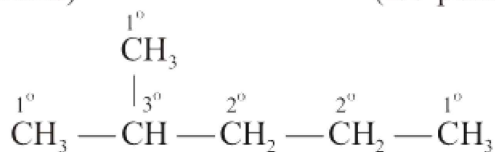
- (ii) Branched chain hydrocarbon having tertiary carbon ( $3^\circ$ ) atom are named as “iso” hydrocarbons. e.g.,



(Iso-butane)

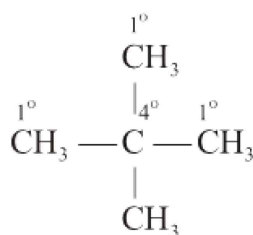


(Iso-pentane)

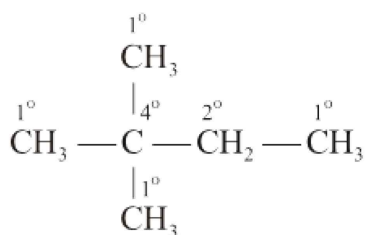


(Iso-hexane)

- (iii) The branched chain hydrocarbons having quaternary carbon atom ( $4^\circ$ ) are named as “neo” hydrocarbons.



(Neo-pentane)



(Neo-hexane)

### COMMON NAMES OF ALKENES

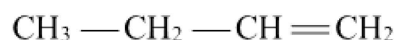
Common name of alkene are formed by replacing “**ane**” of alkane by “**ylene**”. e.g.,



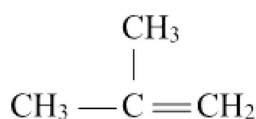
(Ethylene)



(Propylene)



(n-Butylene)



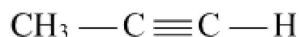
(Iso-butylene)

### COMMON NAMES OF ALKYNE

The first member of alkyne series is acetylene,  $\text{C}_2\text{H}_2$ . All the common name of alkynes are derived from acetylene.



(Acetylene)



(Methyl acetylene)



(Dimethyl acetylene)

The prefixes used in the common names have limited use and cannot be applicable for more complex molecules. Moreover, common names give only minimum information about the structure of compound.

### IUPAC NAMES

In 1889 the solution for naming the organic compounds systematically was brought by international Chemical Congress. A report was accepted in 1892 in Geneva but it was found incomplete. In 1930, international union of chemistry (IUC) gave a modified report which is also referred as Liege Rules. This report was further modified by International Union of Pure and Applied Chemistry (IUPAC) in the year 1947. Since

that date, the union has issued periodic reports on rules for the systematic nomenclature of organic compounds. The most recent of which was published in the year 1979. IUPAC system of nomenclature is based on the following principle.

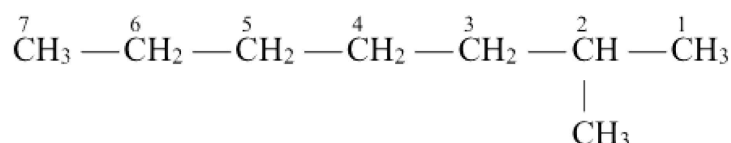
*"Each different compound should have a different name."*

Thus through a systematic set of rules, the IUPAC system provides different names for more than 7 million known organic compounds.

## RULES FOR NAMING ALKANES

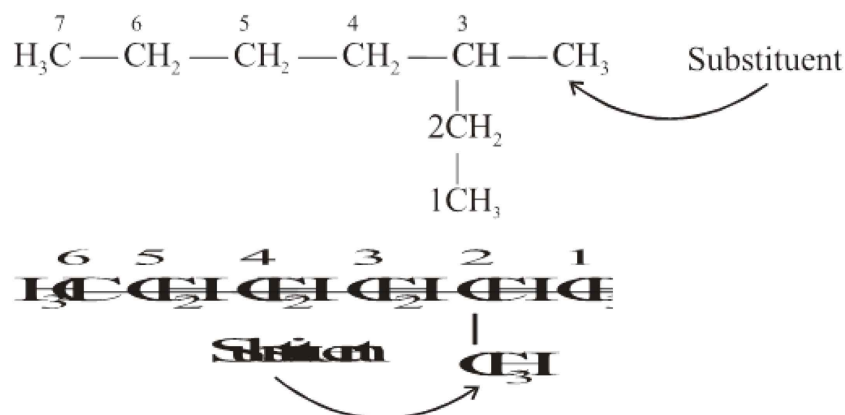
Branched – chain alkanes are named according to the following rules.

- (1) Select longest possible chain of carbon atoms. Length of chain determines the parent name e.g., the longest chain in the given formula is heptane.

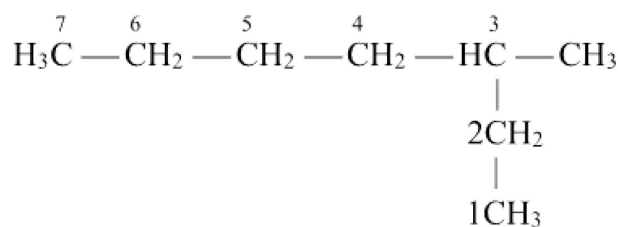


The carbon atoms which are not part of the chain, are called substituent.

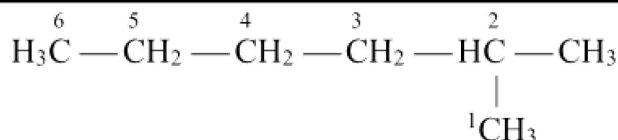
- (2) Start numbering from that end which is near to the substituent.



- (3) Write the location (number at which substituent is attached) and name of substituent before the parent name or stem name. e.g.,

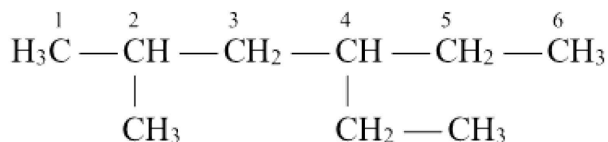


3-Methylheptane



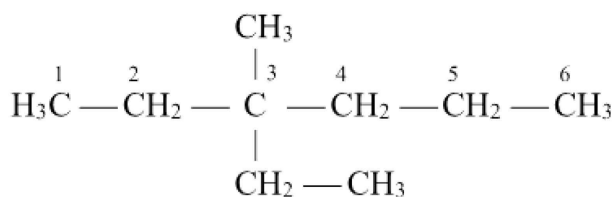
2-Methyl hexane

- (4) If more than one substituents of different types are present, they should be named in alphabetic order. (ethyl before methyl). e.g.,



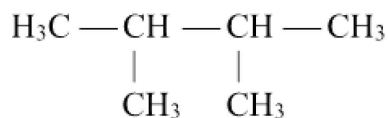
4-Ethyl 2-Methyl hexane

- (5) When two substituents are present at the same carbon, write that number twice.

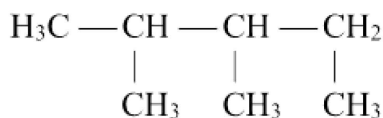


3-Ethyl-3-methylhexane

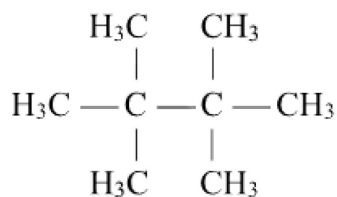
- (6) If similar substituents are present more than once, the number of carbon atom to which substituent is attached given each time. Prefixes di, tri, tetra, etc., are used for the same type of substituents.



2,3-Dimethylbutane

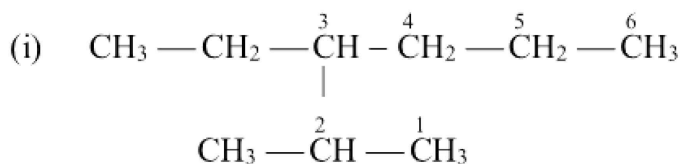


2,3-Dimethylpentane

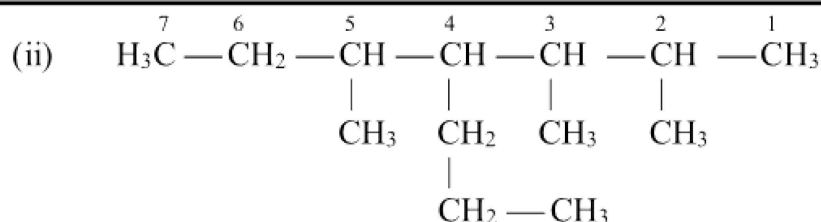


2,2,3,3, Tetramethylbutane

- (7) When two chains of equal length compete for selection as the parent chains, choose the chain with greater number of substituents.

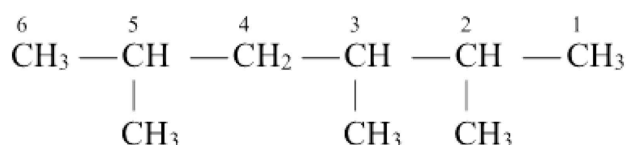


3-Ethyl-2-methyl Hexane (not 3-isopropyl hexane)



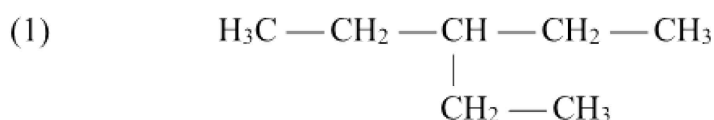
2,3,5-Trimethyl 4-n-propyl heptane

- (8) When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.

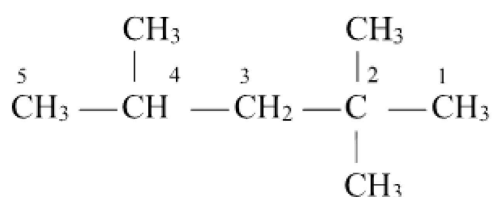
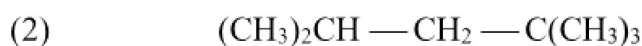


2,3-5-Trimethylhexane (not 2,4,5-trimethylhexane)

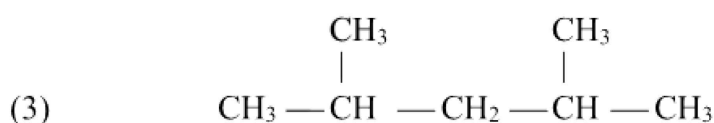
### Some Other Examples of Alakens:



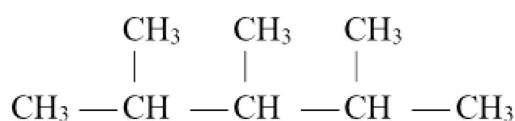
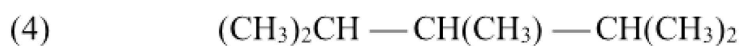
3-Ethyl pentane



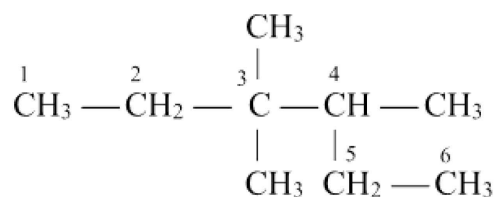
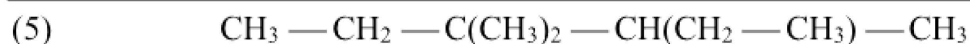
2,2,4-Trimethyl pentane



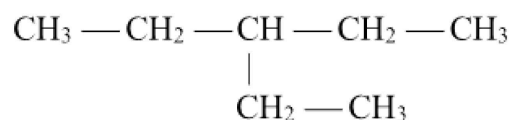
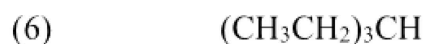
2,4-Dimethyl pentane



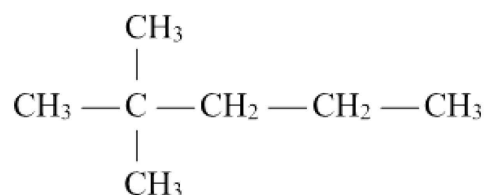
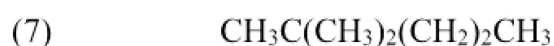
2,3,4-Trimethyl pentane



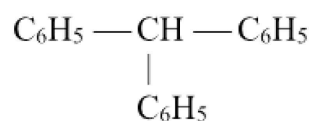
3,3,4 Trimethyl-hexane



3-Ethyl pentane



2,2-Dimethyl pentane

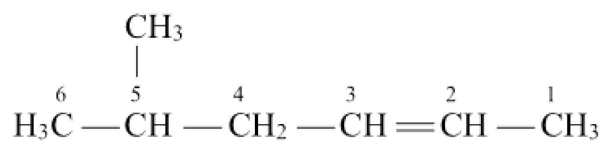


Triphenyl methane

**Note:**  $\text{C}_6\text{H}_5$  is an aryl radical and its name is phenyl.

### RULES FOR NAMING ALKENE

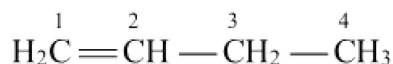
- (1) Select longest possible chain of carbon atoms containing  $\text{C} = \text{C}$  double bond.
- (2) Start numbering from that end which is nearer to the double bond. Suffix of alkene is “ene”. The suffix “ane” of alkanes is changed by “ene” for alkenes.



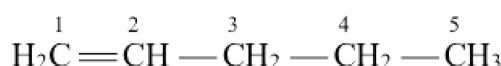
5-Methyl-2-hexene



- (3) Mention the location of the double bond by using the number of the first atom of the double bond as a prefix.

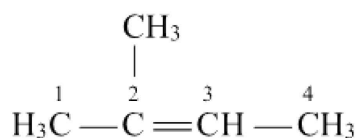


1-Butene

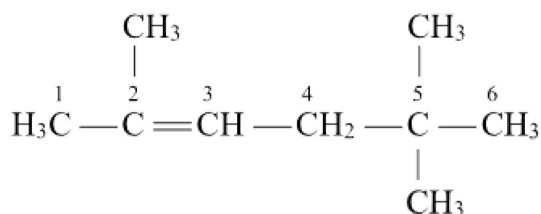


1-Pentene

- (4) Indicate the locations of the substituent groups by the numbers of the carbon atoms to which they are attached.

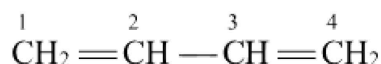


2-Methyl-2-butene

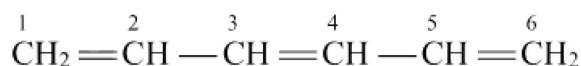


2,5,5-Trimethyl-2-hexene

- (5) If more than one double bonds are present, indicate the prefix diene for two, triene for three double bonds. etc.



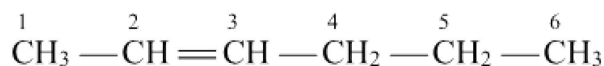
1, 3-Butadiene or Buta-1, 3-diene



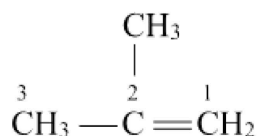
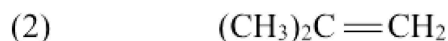
1,3,5-Hexatriene or hexa 1,3,5-triene

### Some Other Examples of Alkenes:

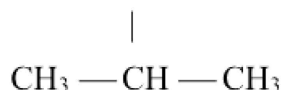
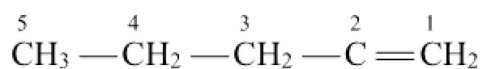
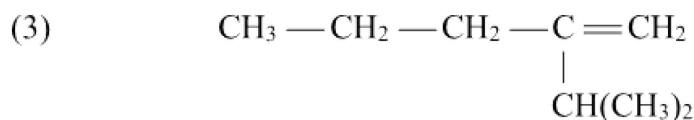
- (1)  $\text{CH}_3-\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$



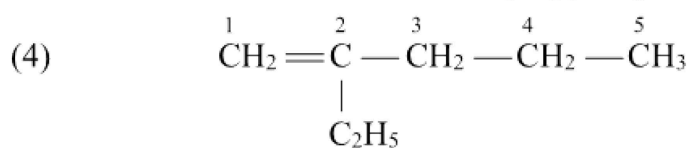
2-Hexene



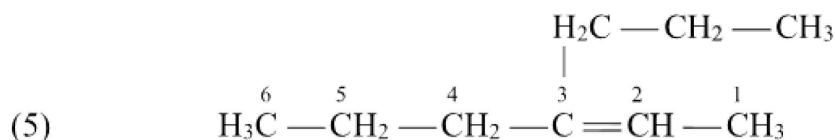
2-Methyl-1-Propene



2-Iso propyl-1-pentene



2-Ethyl-1-pentene



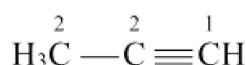
3-n-Propyl 2-hexene

### RULES FOR NAMING ALKYNES

- (1) Select longest possible chain of carbon atoms containing  $\text{C} \equiv \text{C}$  triple bond. The suffix of alkyne is “yne”. The suffix of alkane “ane” is replaced by “yne” for alkynes.

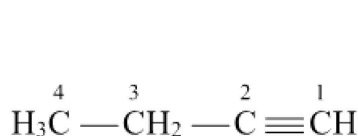


Ethyne

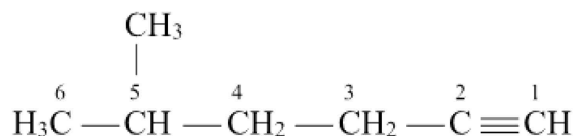


Propyne

- (2) The position of triple bond is shown by numbering the alkyne, so that minimum number is assigned to the triple bond.

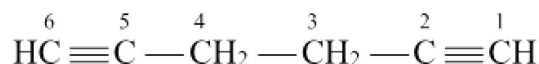


Butyne



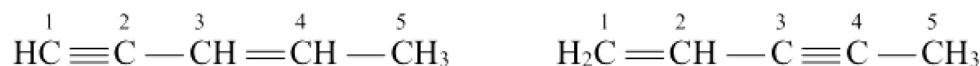
5-Methyl-1-hexyne

- (3) If a hydrocarbon contains more than one triple bonds, it is named as alkadiyne and triyne etc., depending on the number of triple bonds.



Hex-1, 5-diyne or 1, 5-hexadiyne

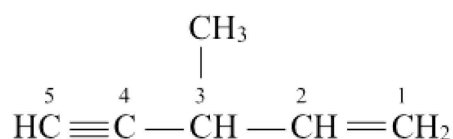
- (4) If both double and triple bonds are present in the compound then ending “en-yne” is given to the root.
- (a) Lowest possible number is assigned to a double or a triple bond irrespective of whether “one” or “yne” gets the lower number.



Pent-3-en-1-yne

Pent-1-en-3-yne

- (b) If double and triple bonds are present at equal position, double bond will be preferred for numbering and naming.



3-Methyl Pent-1-en-4-yne

Suffix of alkene will be “en” instead of “ene” when another functional is also present in a molecule.

### Some Other Examples of Alkynes:

- (1)  $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$

2-Butyne

- (2)  $\begin{array}{ccccccc} 1 & 2 & 3 & 4 & 5 & 6 \\ \text{CH}_2 = \text{CH} - \text{C} \equiv \text{C} - \text{CH} = \text{CH}_2 \end{array}$

Hex 1,5-dien-3-yne

- (3)  $\begin{array}{ccccccc} 1 & 2 & 3 & 4 & 5 & 6 \\ \text{CH} \equiv \text{C} - \text{CH} = \text{CH} - \text{C} \equiv \text{CH} \end{array}$

Hex-3-en-1,5-diyne

- (4)  $\begin{array}{cccc} 1 & 2 & 3 & 4 \\ \text{CH}_2 = \text{CH} - \text{C} \equiv \text{CH} \end{array}$

But-1-en-3-yne

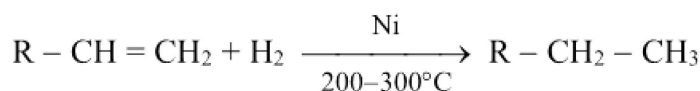
## ALKANES OR PARAFFINS

Alkanes are saturated hydrocarbons with general formula  $C_nH_{2n+2}$ . Methane ( $CH_4$ ) is the simplest member of this family. Each carbon atom of saturated hydrocarbon is  $sp^3$ -hybridized with tetrahedral geometry.

### GENERAL METHOD FOR PREPARATIONS

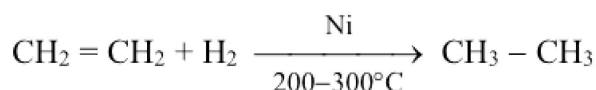
**(1) Hydrogenation of unsaturated hydrocarbons (Sabatier's and Sendern's reaction):**

Hydrogenation of alkenes or alkynes in the presence of Nickel catalyst at  $200-300^\circ C$  yields alkanes. e.g.,



Alkene

Alkane

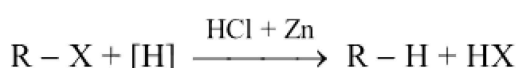
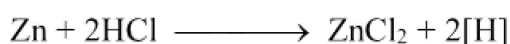


The hydrogenation can also be carried out with platinum or palladium at room temperature but they are expensive than Nickel.

This method is of industrial importance. Production of vegetable ghee by the catalytic hydrogenation of vegetable oil (unsaturated fatty acids) is an example of the application of this method on industrial scale.

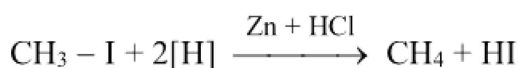
**(2) From Alkyl Halides:**

**(a)** An alkane is produced when an alkyl halide reacts with zinc in the presence of an aqueous acid such as  $HCl$  or  $CH_3COOH$ .



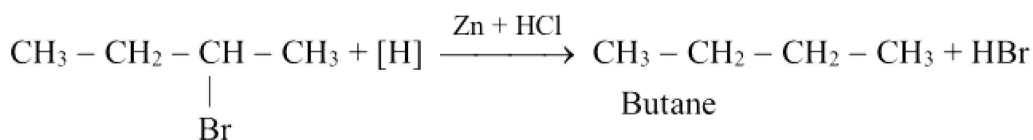
Alkyl halide

Alkane

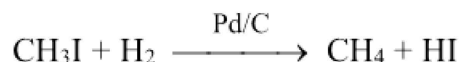
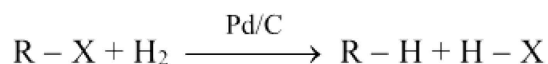


Methyl iodide

Methane

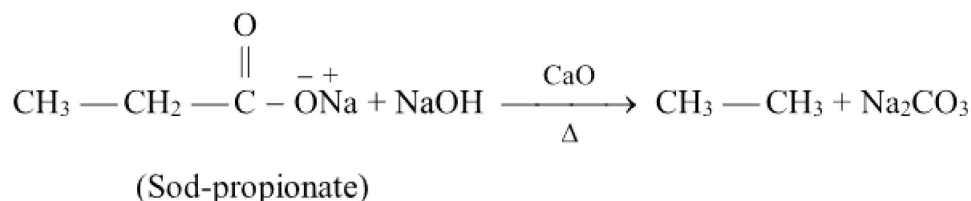
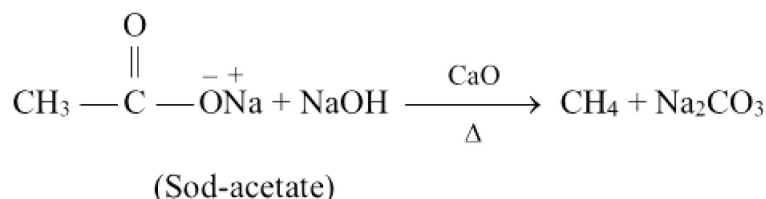
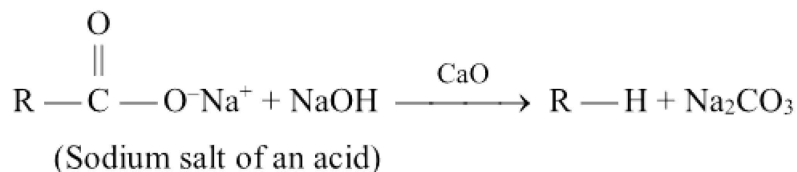


- (b) **Hydrogenolysis:** Alkanes can also be prepared from alkyl halides using palladium charcoal as a catalyst. The method is known as Hydrogenolysis (hydrogenation which takes place by cleavage of H-H bond).

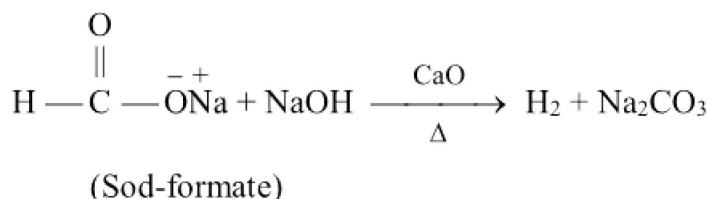


(3) **Decarboxylation of Mono-carboxylic Acids:**

- (a) When sodium salts of fatty acids are heated with soda-lime (prepared by soaking quick lime (CaO) with caustic soda solution and drying the product). They eliminate a molecule of CO<sub>2</sub> to form alkanes except sodium formate which forms H<sub>2</sub>.

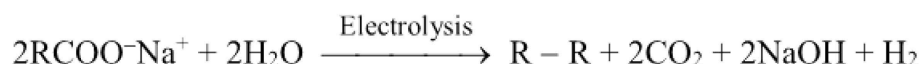


**Note:** Sodium formate forms hydrogen



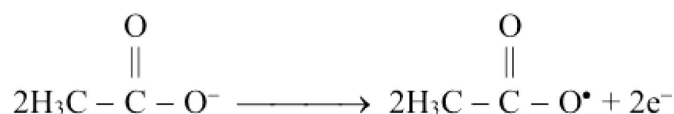
(b) **Kolbe's Electrolytic Method:**

When a concentrated solution of sodium or potassium salt of a mono carboxylic acid is electrolysed, an alkane is produced. This method is only suitable for the preparation of symmetrical alkanes i.e., those of the type R - R. Methane cannot be prepared by this method.

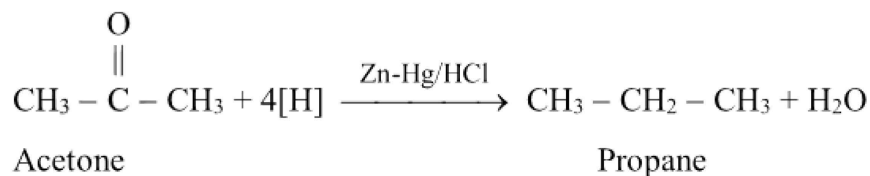


**Mechanism:**

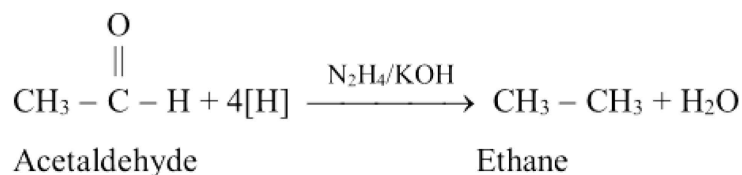
When potassium salt of acetic acid is electrolysed, acetate ions migrate towards the anode gives up one electron to produce free radical ( $\text{CH}_3\text{COO}^\bullet$ ), which decomposes to give a methyl free radical ( $\text{CH}_3^\bullet$ ) and  $\text{CO}_2$ . Two such methyl radicals combine to give ethane.

**At Anode:****At Cathode:****(4) From Aldehyde and Ketones (Carbonyl Compounds):****(a) Clemensen Reduction:**

In this reaction, ketones react with zinc amalgam and hydrochloric acid to form alkane (an alloy containing mercury as one of the components is called amalgam).

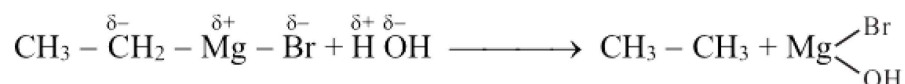
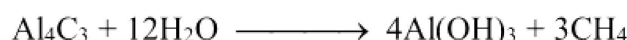
**(b) Wolf Kishner's Reduction:**

Aldehyde reacts with KOH and hydrazine and changes to alkane.



**(5) From Grignard Reagent:**

Alkyl halides react in anhydrous ether with magnesium to form alkyl magnesium halides, known as Grignard Reagent. They decompose on treatment with water or dilute acid to give alkanes.

**(6) Hydrolysis of  $\text{Al}_4\text{C}_3$  (method for methane only):**
**PHYSICAL CHARACTERISTICS OF ALKANES**

- (1) Alkanes containing upto four carbon atoms are colourless, odourless **gasses** while pentane to heptadecane ( $\text{C}_5$  to  $\text{C}_{17}$ ) are colourless **liquids**. The higher members from  $\text{C}_{18}$  onwards are **waxy solids** which are also colourless and odourless.
- (2) Alkanes are **non-polar** or very weakly polar and are insoluble in polar solvents like water, but soluble in non-polar solvents like benzene, ether, carbon tetrachloride, etc.
- (3) Their physical constants like boiling points, melting points, density etc., increase with the increase in number of carbon atoms, whereas solubility decreases with increase in molecular mass. The boiling point increases by  $20^\circ\text{C}$  to  $30^\circ\text{C}$  for addition of each  $\text{CH}_2$  group to the molecule.

The boiling points of alkanes having **branched chain** structures are **lower** than their isomeric normal chain alkanes, e.g., n-butane has a higher boiling point ( $-0.5^\circ\text{C}$ ) than isobutane ( $-11.7^\circ\text{C}$ ) B.P of n-pentane =  $36^\circ\text{C}$ , Isopentane =  $28^\circ\text{C}$ , Neopentane =  $9.5^\circ\text{C}$  and Melting point of n-pentane =  $-130^\circ\text{C}$ .

and M.P. of Iso-pentane  $-160^\circ\text{C}$

M.P. of Neo-pentane  $-17^\circ\text{C}$

**Straight chain alkanes** have **greater polarizability** than branched chain alkanes and have greater intermolecular forces in them.

- (4) The melting points and boiling points of alkanes also increases with the increase in molecular masses but this increase is not so regular.

## REACTIVITY OF ALKANES

The alkanes or paraffins (Latin: parum = little, affins = affinity) under ordinary condition are inert towards acids, alkalis, oxidizing agents and reducing agents. However, under suitable conditions, alkanes do undergo two types of reactions.

- (i) Substitution reactions
- (ii) Thermal and catalytic reactions

These reactions take place at high temperature or on absorption of light energy through the formation of highly reactive free radicals.

Non-reactivity of alkanes is due to the following reasons:

### (1) Non-polar Nature of C – H Bond:

The reactivity of alkanes under normal conditions may be explained on the basis of the non-polarity of the bonds forming them. The electronegativity values of carbon (2.5) and hydrogen (2.1) do not differ appreciably from the ionic reagents such as acids, alkalies, oxidizing agents, etc., and find no reaction site in the alkane molecules to which they could be attached.

### (2) Inertness of $\sigma$ -bond:

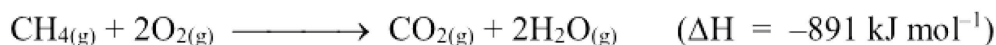
The un-reactivity of alkanes can also be explained on the basis of inertness of a  $\sigma$ -bond. In a  $\sigma$ -bond the electrons are very tightly held between the nuclei and electrons present in a  $\sigma$ -bond can neither attack on any electrophile nor a nucleophile can attack on them. Both these facts make alkanes less reactive.

## REACTIONS OF ALKANES

### (1) Combustion:

Burning of an alkane in presence of oxygen is known as **Combustion**.

Complete combustion of an alkane yields  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and heat. “*The amount of heat evolved when one mole of a hydrocarbon is burnt to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is called heat of combustion.*” e.g.,



Although the reaction is highly exothermic, it required very high temperature to initiate it, e.g., by a flame or a spark.

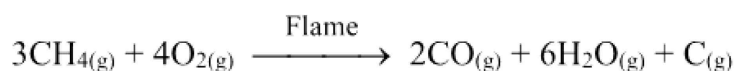
Combustion is the major reaction occurring in the internal combustion engines of automobiles. A compressed mixture of alkanes and air burns smoothly in the internal combustion engine and increases its efficiency.



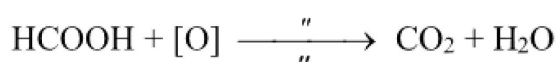
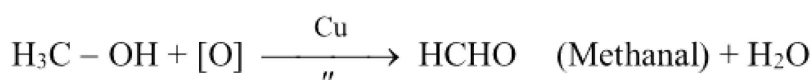
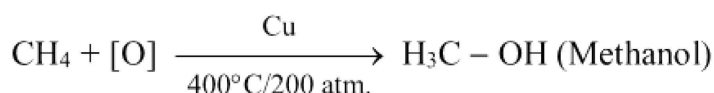
**(2) Oxidation:**

Oxidation of methane under different conditions give different products.

- (i) Incomplete oxidation occurs in a limited supply of oxygen or air and results in the formation of CO and carbon black.



- (ii) **Catalytic Oxidation:** Lower alkanes when burnt in the presence of metallic catalysts, at high temperature and pressure results in the formation of useful products.



Catalytic oxidation of alkanes is used industrially to prepare higher fatty acids used in soap and vegetable oil industries.

**(3) Nitration:**

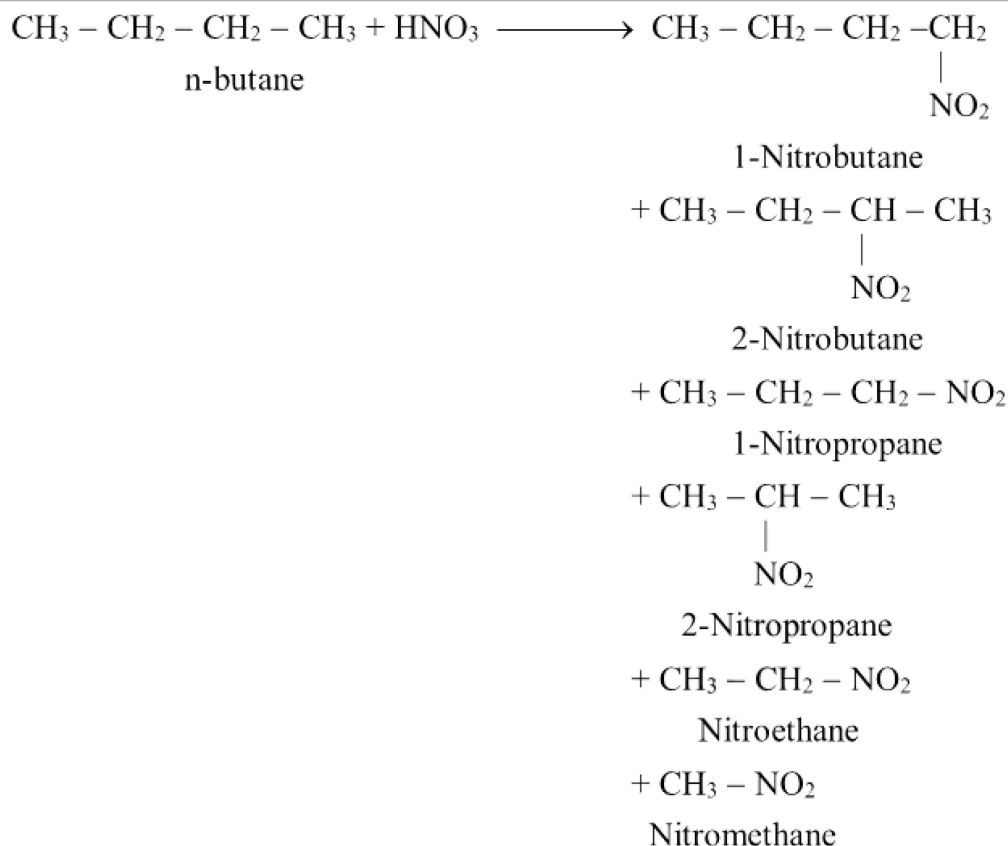
It is a substitution reaction of alkanes in which a hydrogen atom of an alkanes is replaced by nitro group ( $-\text{NO}_2$ ). Alkanes undergo vapour-phase nitration under drastic condition (at  $400\text{--}500^\circ\text{C}$ ) to give nitroalkanes. e.g.,



Nitromethane

Nitroalkanes generally find use as fuels, solvents, and in organic synthesis.

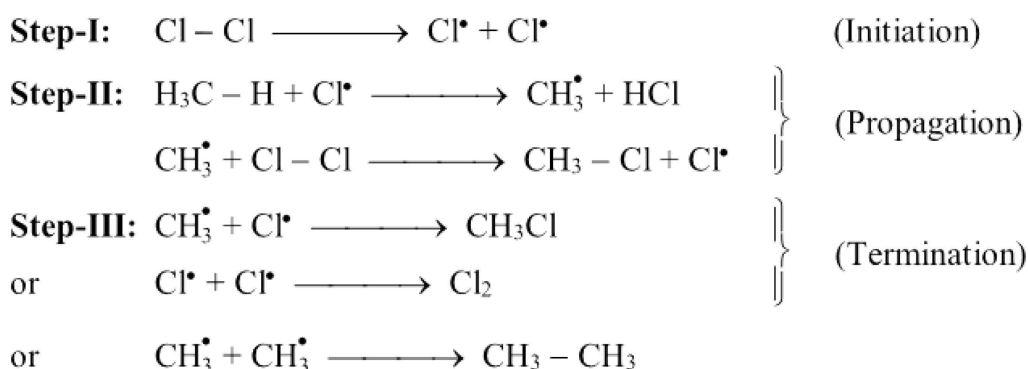
Nitration of higher alkanes forms number of nitro-alkanes due to cracking. It is called vapour-phase nitration. For example:



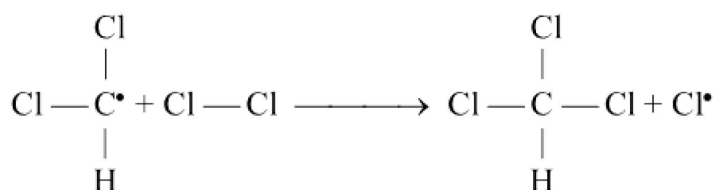
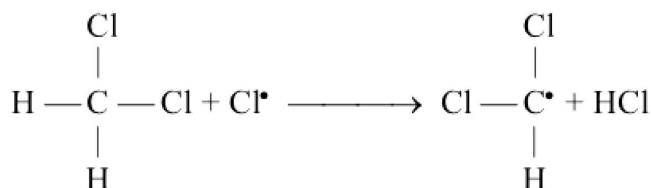
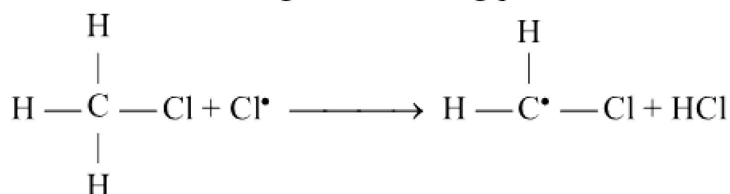
**(4) Halogenations (Substitution Reaction):**

Alkanes react with chlorine and bromine in the presence of sunlight or UV light or at high temperature resulting in the successive replacement of hydrogen atoms with halogens called **substitution**. Extent of halogenations depends upon the amount of halogen used. If halogen and alkanes are taken with 1 : 1 ratio  $\text{CH}_3\text{Cl}$  is formed. If greater amount of halogen is used, further substitution of halogen will also takes place.

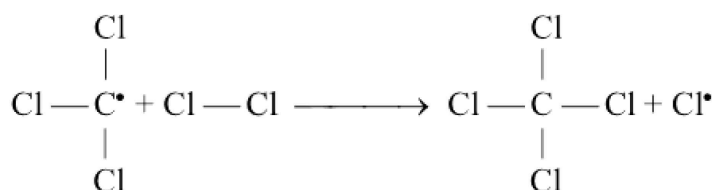
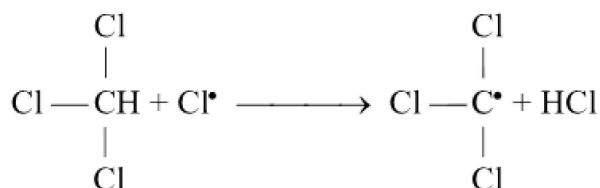
Reaction of alkanes with fluorine is highly violent and results in a mixture of carbon, fluorinated alkanes and hydrofluoric acid. Iodine does not substitute directly because the reaction is too slow and reversible. The order of reactivity of halogens is  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .



By further substitution of halogens, following products are obtained.



Chloroform or trichloromethane



Tetrachloromethane or carbon tetrachloride

#### Uses of Methane:

- (1) Methane is used for the preparation of methyl chloride ( $\text{CH}_3\text{Cl}$ ), methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), chloroform ( $\text{CHCl}_3$ ) and carbon tetrachloride ( $\text{CCl}_4$ ).
- (2) Methane is important constituent of natural gas and used as fuel.
- (3) Methane is used for the industrial preparation of methyl alcohol ( $\text{CH}_3\text{OH}$ ), formaldehyde ( $\text{HCHO}$ ) and formic acid ( $\text{HCOOH}$ ).
- (4) Methane is used for preparation of carbon black used in paint, printing inks and automobile tyres.
- (5) By cracking of methane hydrogen gas is produced. This gas is used for the manufacture of vegetable ghee and fertilizers.
- (6) In the manufacture of urea.

## ALKENES

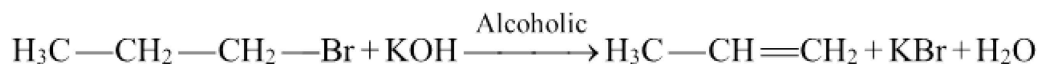
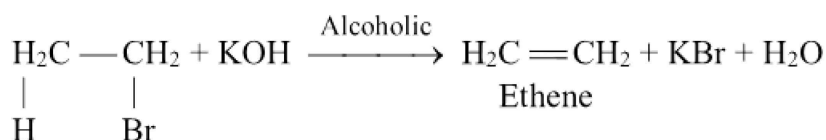
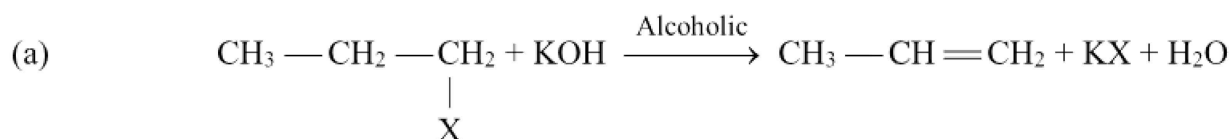
Alkenes have two hydrogen atoms less than the corresponding saturated hydrocarbons. They are also known as Olefins (derived from Latin word olefins meaning oil forming) because lower members form oily products on treatment with chlorine or bromine. The simplest olefin is  $C_2H_4$ , ethene.

Alkenes having one double bond are known as mono-enes with general formula  $C_nH_{2n}$ . Alkenes containing two double bonds are called dienes.

### GENERAL METHODS OF PREPARATION

#### (1) Dehydrohalogenation of Alkyl Halides (Elimination Reaction):

Alkyl halides on heating with alcoholic potassium hydroxide undergo dehydrohalogenation i.e., elimination of a halogen atom together with a hydrogen atom from adjacent carbon atoms.

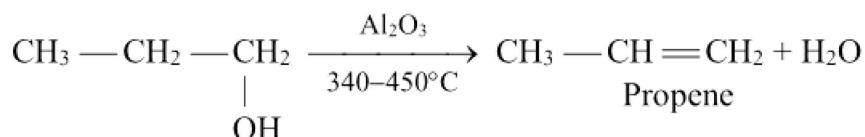


(b) **Note:** With aqueous KOH, alcohols are formed:



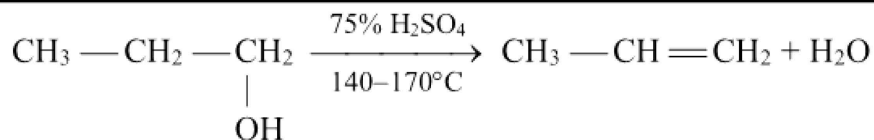
#### (2) Dehydration Alcohols:

Alcohols when dehydrated in the presence of a catalyst give alkenes. The best procedure is to pass vapours of alcohol over heated alumina.

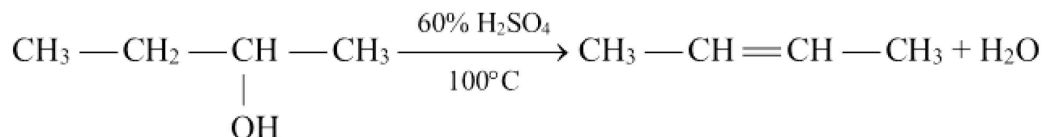


$\text{Al}_2\text{O}_3$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{H}_2\text{SO}_4$  (conc.),  $\text{H}_3\text{PO}_4$  are dehydrating agents used for preparation of alkenes. The ease of dehydration of various alcohols is in the order.

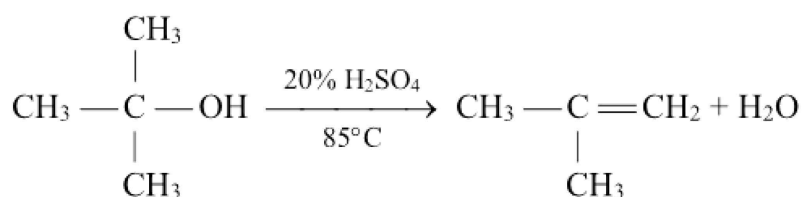
Ter. alcohol > Sec. alcohol > Pri-alcohol



Primary alcohol



Secondary alcohol

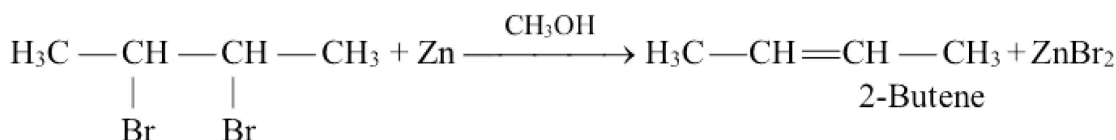
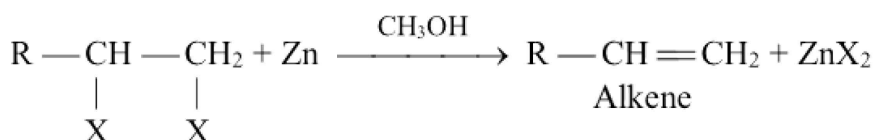


Ter-alcohol

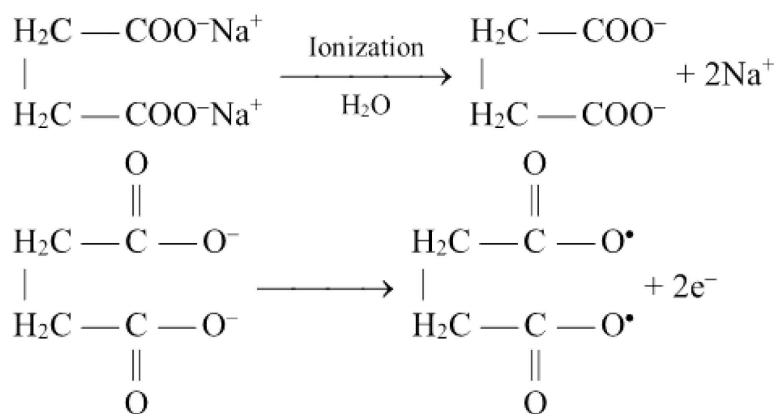
Isobutylene

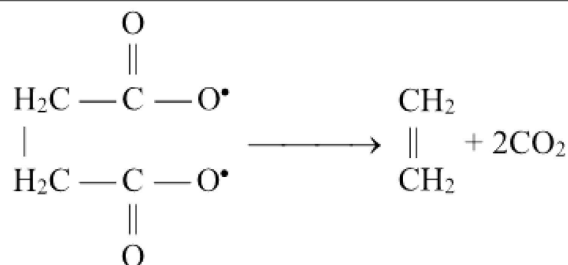
**(3) Dehalogenation of Vicinal Dihalides:**

Vic-dihalides have halogens on adjacent carbon atoms. Dehalogenation occurs when dihalide is treated with zinc dust in an anhydrous solvent like methanol or acetic acid.

**(4) Electrolysis of Salts of Dicarboxylic Acid (Kolbe's Electrolytic Method)**

When sodium or potassium salts of the dicarboxylic acid like succinic acid are subjected to electrolysis in an aqueous solution, alkenes are formed.



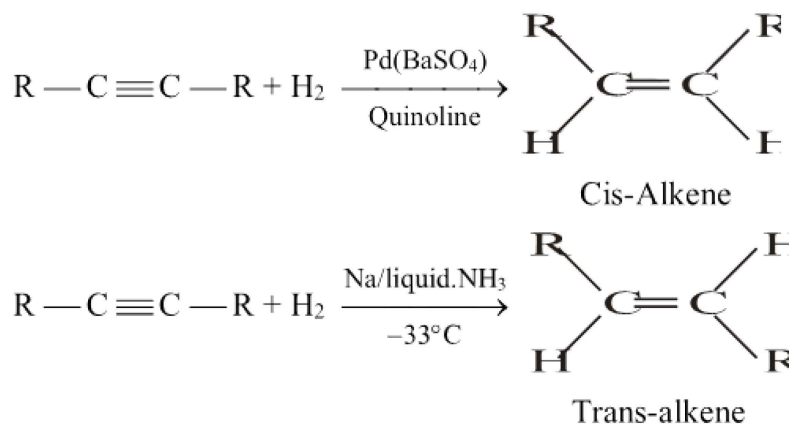


**At Cathode:**



**(5) Partial Hydrogenation of Alkyne:**

Controlled hydrogenation of alkynes with hydrogen gas in an equi-molar ratio over heated catalysts, gives alkenes. The catalyst is finely divided palladium supported on  $\text{BaSO}_4$  and poisoned by treatment with quinoline (Lindler's catalyst).



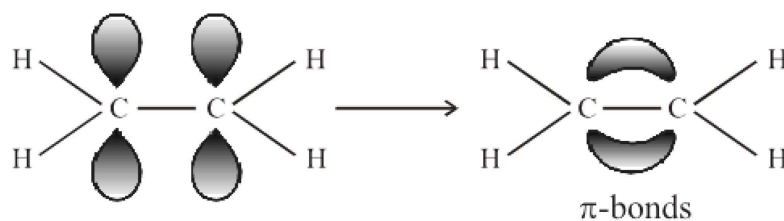
### PHYSICAL CHARACTERISTICS

- (1) First three members i.e., ethene, propene and butene are gases at room temperature while  $\text{C}_5$  to  $\text{C}_{15}$  are liquids and the higher members are solids.
- (2) They are insoluble in water but soluble in alcohol.
- (3) They have characteristic smell and burn with luminous flame.
- (4) Unlike alkanes, they show weakly polar properties because of  $\text{sp}^2$  hybridization.

### REACTIVITY OF ALKENES

In alkenes, double bond is present between two carbon atoms, one is sigma and other is  $\pi$ -bond,  $\sigma$ -bond is formed by linear overlapping of partially filled  $\text{sp}^2$  hybrid orbitals and electron density is maximum between two nuclei or at bond axis.  $\pi$ -bond is

formed by the parallel overlapping of p-orbitals of carbon atoms. In  $\pi$ -bond, electron density is maximum above and below the bond axis. Due to less overlapping  $\pi$  electrons are not firmly attached. Due to less overlapping region  $\pi$ -bonds are weaker bond than sigma bonds.  $\pi$ -electrons are more exposed electrons and an electrophile (electron deficient specie) can attack easily on  $\pi$ -electrons. Thus the compounds containing  $\pi$ -bond are more reactive than alkane. Alkenes usually undergo addition reactions.



## REACTIONS OF ALKENES

### (a) Addition Reactions:

#### (1) Hydrogenation (addition of hydrogen):

Hydrogenation is a process in which a molecule of hydrogen is added to an alkene in the presence of a catalyst and at moderate pressure (1-5 atm) to give a saturated compound. The process is known as catalytic hydrogenation.

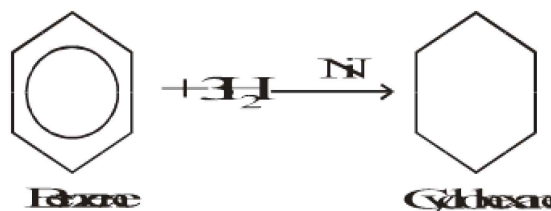
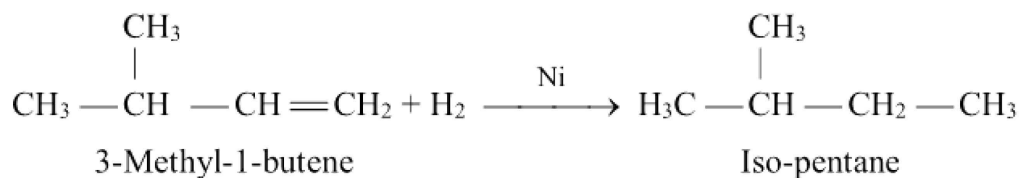
It is a highly exothermic process and the amount of heat evolved when one mole of an alkene is hydrogenated is called heat of hydrogenation. The heat of hydrogenation of most alkenes is about  $120 \text{ kJ mole}^{-1}$  for each double bond present in a molecule. The catalysts used are Pt, Pd or Raney Nickel.

#### Raney Nickel:

It is prepared by treating a Ni — Al alloy with caustic soda.



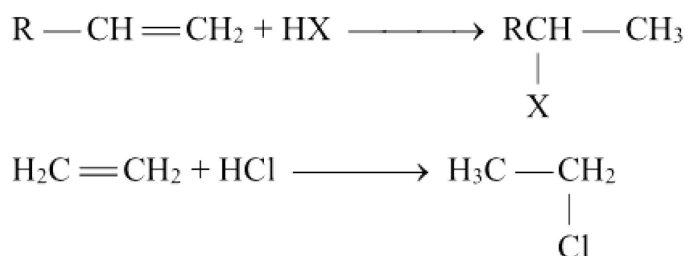
Most alkenes are hydrogenated over Raney Nickel at about  $100^\circ\text{C}$  and 3-atmospheric pressure.



Catalytic hydrogenation of alkenes is used in the laboratory as well as in industry. In industry, it is used for the manufacture of **vegetable ghee** from vegetable oils. In the laboratory, it is used to synthesize many chemicals like alkane or cycloalkane. Hydrogenation is also used to determine the degree of unsaturation of compound.

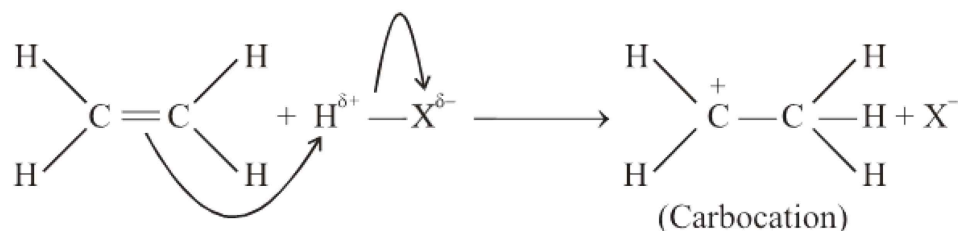
## (2) Addition of Hydrogen Halides:

Alkenes react with aqueous solution of halogen acids to form alkyl halides. The order or reactivity of halogen acids is  $\text{HI} > \text{HBr} > \text{HCl}$ .

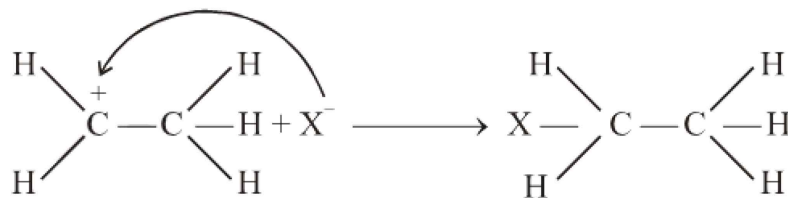


### Mechanism:

The addition of a hydrogen halides to an alkene takes place in two steps. Alkene accepts the proton of hydrogen halide to form a carbocation.



The carbocation then reacts with the halide ion, to form alkyl halide.

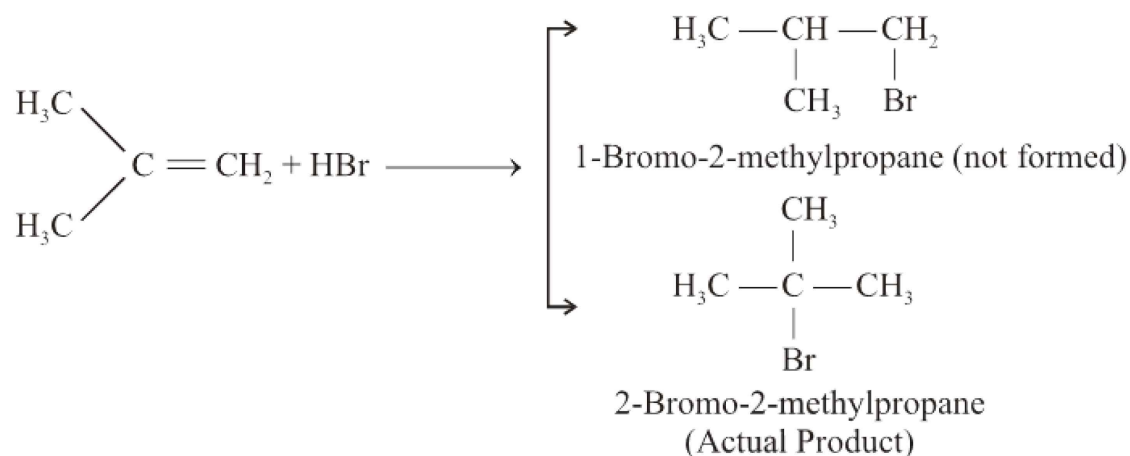
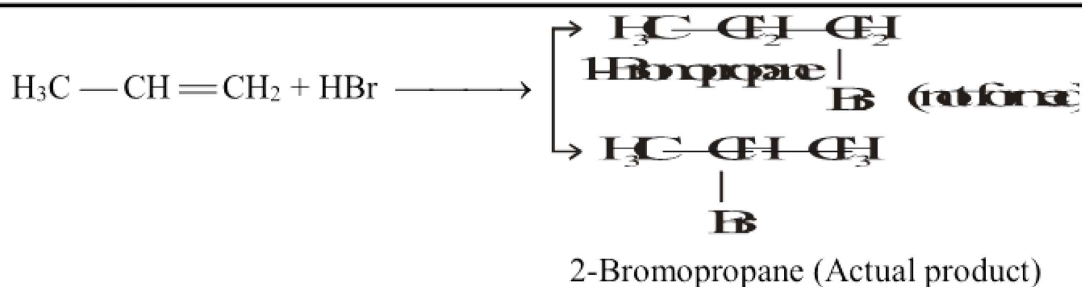


### Markownikov's Rules:

*"If unsymmetrical reagent is added to unsymmetrical alkene, the negative part of reagent will be added to that carbon which have least number of hydrogen atoms."*

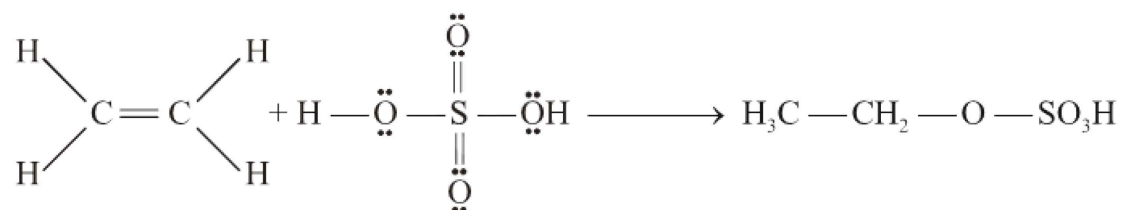
Unsymmetrical alkenes are those which have different number of hydrogen on both side of double bond.



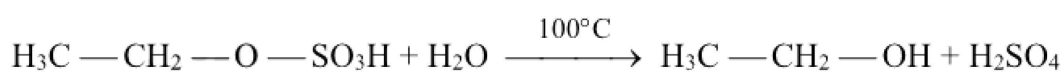


### (3) Addition of Sulphuric Acid:

When alkenes are treated with cold concentrated sulphuric acid, they are dissolved because they react by addition to form alkyl hydrogen sulphate.

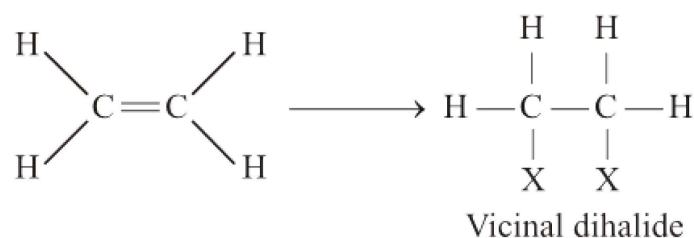


This alkyl hydrogen sulphates on boiling with water decomposes give corresponding alcohols. It is called “hydration”.



### (4) Addition of Halogens:

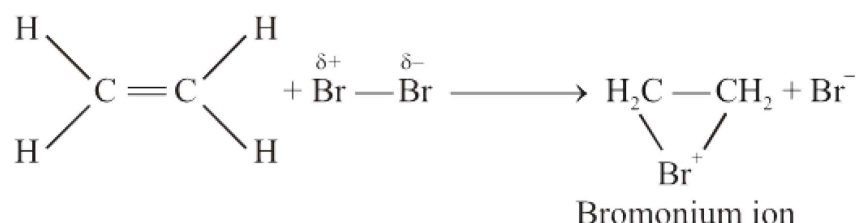
The alkenes on reacting with halogen in an inert solvent like carbon tetrachloride at room temperature, give vicinal dihalides or 1, 2 dihalogenated products.



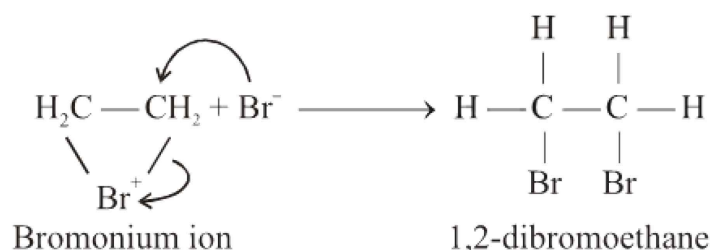
$\text{Br}_2$  and  $\text{Cl}_2$  are effective electrophilic reagents. Fluorine is too reactive to control the reaction. Iodine does not react.

### Mechanism:

- (a) A bromine molecule becomes polarized as it approaches the alkene. This polarized bromine molecule transfers a positive bromine atom to the alkene resulting in the formation of a bromonium ion.



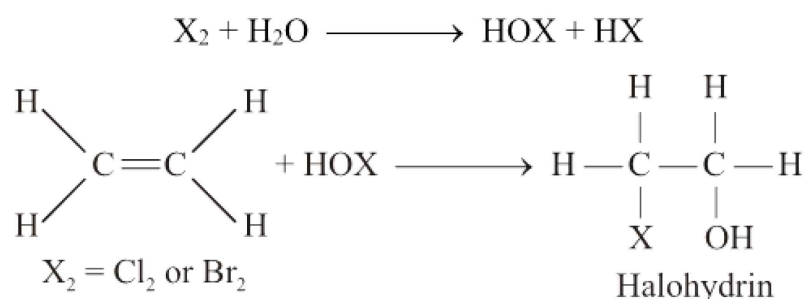
- (b) The nucleophilic bromide ion then attacks on the carbon of the bromonium ion to form vicinal dibromide and the colour of bromine is discharged.



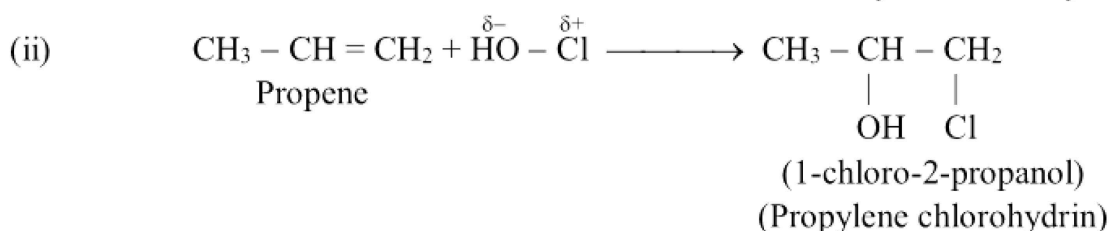
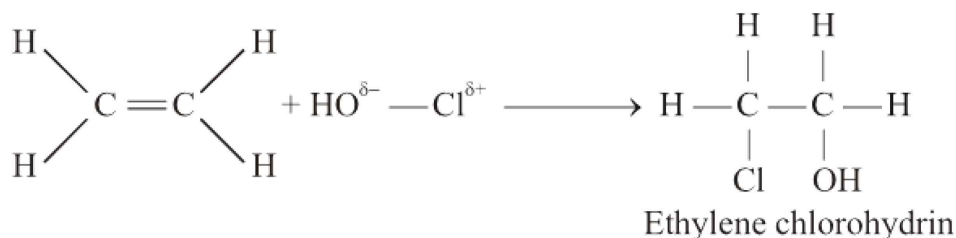
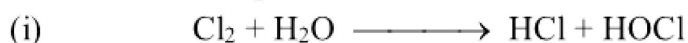
This test is used for the detection of a double bond or detection of unsaturation of a compound.

### (5) Addition of Hypohalous Acid (HOX):

If the halogenation of an alkene is carried out in an aqueous solution, halo alcohol is formed called a Halohydrin. In this reaction, molecules of the solvent also become reactants.



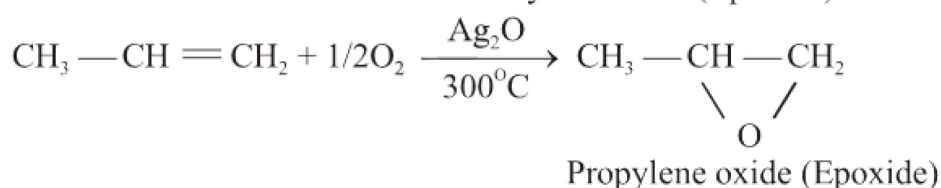
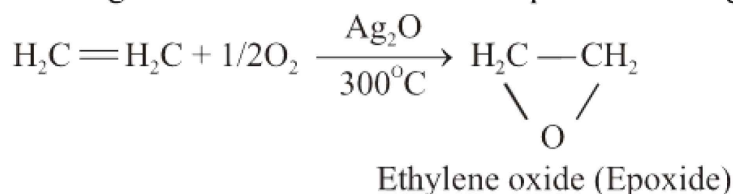
For example:



## (b) Oxidation Reactions:

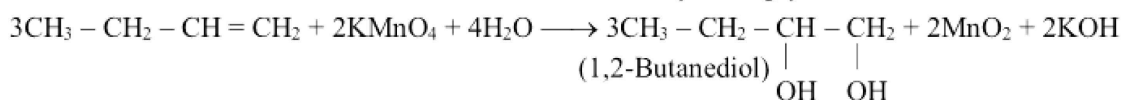
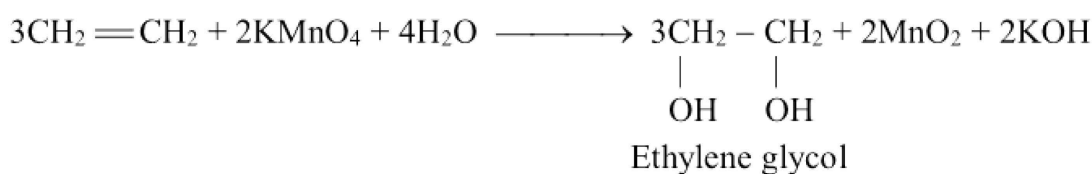
### (1) Addition of Oxygen:

Alkenes when mixed with oxygen or air and passed over a silver catalyst at high temperature and pressure, add an atom of oxygen to form epoxides. Epoxides serve as the starting substances for the industrial production of glycols.



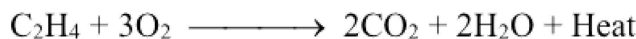
### (2) Hydroxylation (Baeyers Test):

When alkenes are treated with mild oxidizing reagents like dilute (1%) alkaline  $\text{KMnO}_4$  solution (Baeyer's Reagent) at low temperature, hydroxylation of double bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols. The pink colour of  $\text{KMnO}_4$  solution is discharged during the reaction. It is also a test for the presence of unsaturation in the molecules.

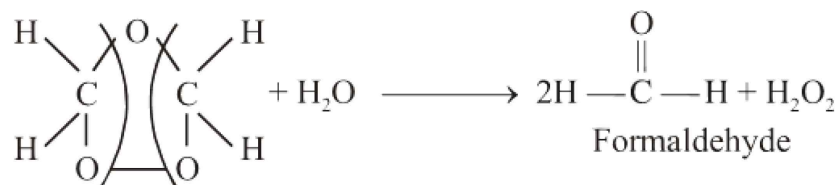
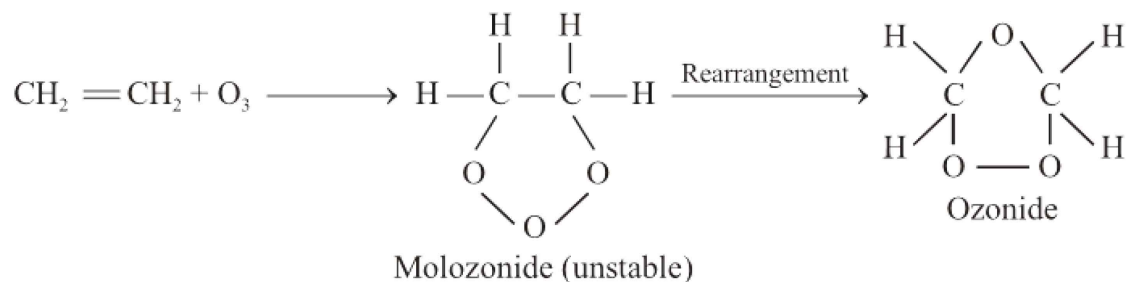


**(3) Combustion:**

Alkenes burn in air with luminous flame and produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$  vapours. Ethene forms a highly explosive mixture with air oxygen.

**(4) Ozonolysis:**

Ozone ( $\text{O}_3$ ) is a highly reactive allotropic form of oxygen. It reacts vigorously with alkenes to form unstable molozonide. It rearranges spontaneously to form an ozonide.



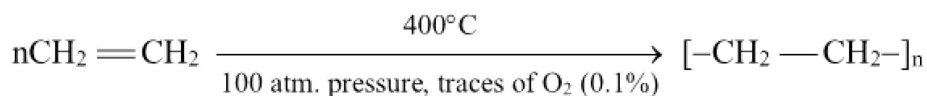
Ozonolysis is used to locate the position of double bond in an alkene.

In the ozonolysis of propene, one molecule of formaldehyde and one molecule of acetaldehyde is formed and ozonolysis of 2-butene forms two molecules of acetaldehyde.

**(c) Polymerization:**

*“In this process small organic molecules (monomers) combine together to form larger molecules known as Polymers.”*

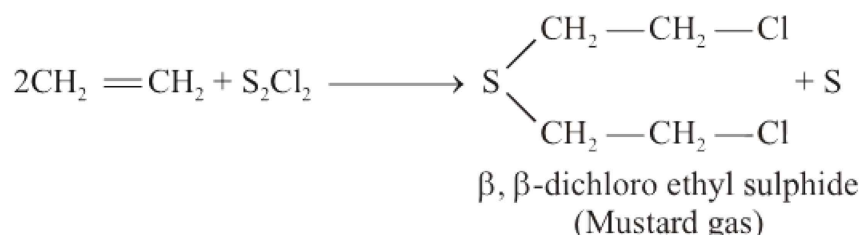
Ethene at  $400^\circ\text{C}$  and 100 atm. pressure, polymerize to polythene or polyethylene.



A good quality polythene is obtained, when ethene is polymerized in the presence of aluminium triethyl  $\text{Al}(\text{C}_2\text{H}_5)_3$  and titanium tetrachloride catalysts ( $\text{TiCl}_4$ ).

## USES OF ETHENE

- (1) Ethene is used for the manufacture of polyethene plastic for making, toys, cable insulations, bags, boxes, plastic utensils, etc.
- (2) Ethene can also be used for the artificial ripening of fruits.
- (3) It is used as general anesthetic in hospitals.
- (4) It is used for the preparation of mustard gas. Mustard gas was used in first world war (1914–1918) by German and his allies. The name of the gas is due to its mustard odor. It is not a gas but a high boiling liquid that is dispersed as mist of tiny droplets. It is a powerful **vesicant or blistering agent**.



- (5) It is used as a starting material for a large number of chemicals of industrial use such as glycols (antifreeze), ethyl halide, ethyl alcohol, etc.

## ALKYNES

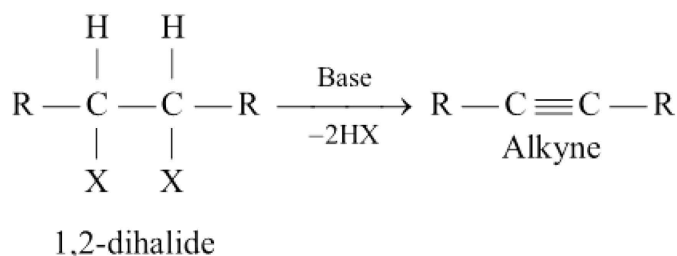
Unsaturated hydrocarbons which contain a triple bond are called Alkynes. They have the general molecular formula  $\text{C}_n\text{H}_{2n-2}$  and contain two hydrogen atoms less than the corresponding alkenes.

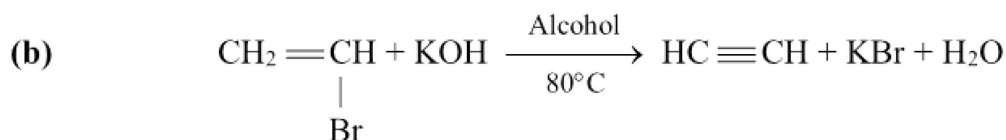
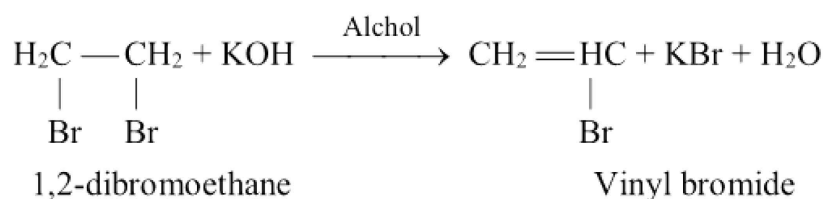
The first member of the Alkyne series has the formula  $\text{C}_2\text{H}_2$  and is known as Ethyne or Acetylene.

### General Methods of Preparation:

#### (1) Dehydrohalogenation of Vicinal Dihalides:

Vicinal dihalide on treatment with a strong base, eliminates two molecules of hydrogen halides from two adjacent carbons to give an alkyne.

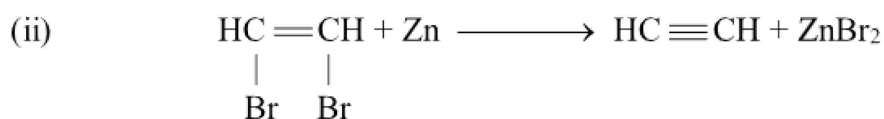
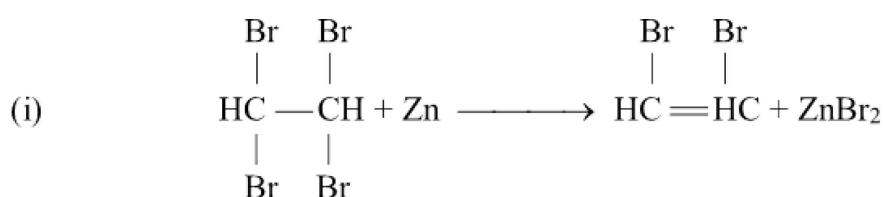


**(a) Mechanism:**

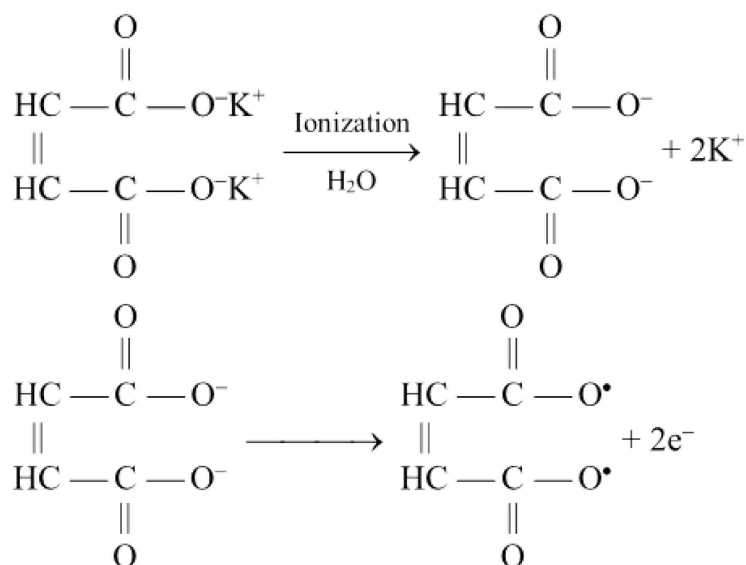
The second molecule of hydrogen halide is removed with great difficulty and requires drastic conditions.

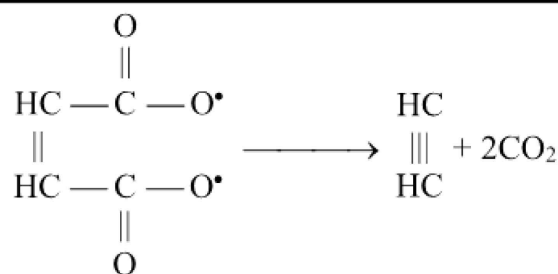
**(2) Dehalogenation of Tetra Halides:**

Tetra haloalkanes on treatment with active metals like Zn, Mg, etc. form alkynes.

**(3) Electrolysis of Salts of Unsaturated Dicarboxylic Acids:**

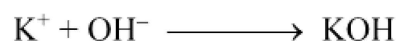
Kolbe's electrolytic method involved electrolysis of aqueous solution of Na or K salts of unsaturated dicarboxylic acids. Electrolysis of aqueous solution of potassium fumarate, give ethyne.





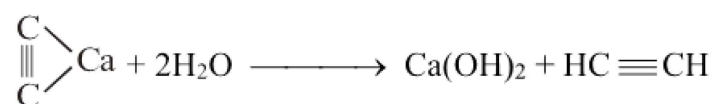
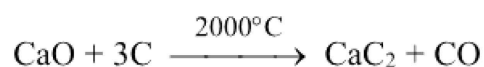
At cathode

Ethyne

**(4) Industrial Preparation (For Acetylene only):**

On industrial scale ethyne is prepared by the reaction of calcium carbide ( $\text{CaC}_2$ ) with water.

Calcium carbide is prepared by heating lime ( $\text{CaO}$ ) and coke ( $\text{C}$ ) at a very high temperature in an electric furnace.



Calcium carbide

Ethyne

**PHYSICAL CHARACTERS OF ALKYNES**

- (1) They are colourless, odourless, except acetylene which has a garlic like odour.
- (2) The first three members are gases (ethyne, propyne and butyne) at room temperature. The next eight members are liquids and higher members are solids.
- (3) The melting points, boiling point and densities increase gradually with the increase in molecule masses.
- (4) They are non-polar and dissolve readily in solvents like ether, benzene and carbon tetra chloride.

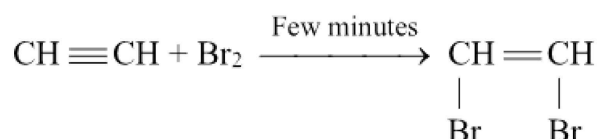
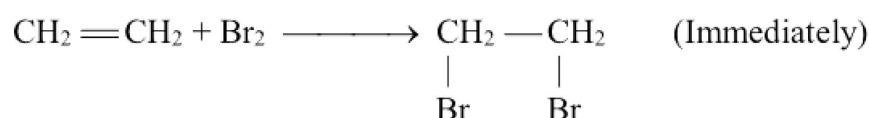
**REACTIVITY OF ALKYNES**

In alkynes, triple bond is present between carbon atoms; one sigma bond and two  $\pi$ -bonds. In sigma bond, electron density is maximum between the nuclei and in  $\pi$ -bond electron density is all around the bond axes. Electron density between triple bonded carbon atoms is very high which draws atoms very close to each other. The  $\text{C} - \text{C}$  bond



distance in triple bond is short than single bond.  $\pi$ -electrons of the triple bond are less exposed due to greater attraction. Alkynes give addition reactions with electrophilic reagents but they have less reactivity than alkenes.

Ethene discharge the colour of  $\text{Br}_2$  immediately while ethyne reacts slowly with  $\text{Br}_2$  and colour of  $\text{Br}_2$  discharge after few minutes.



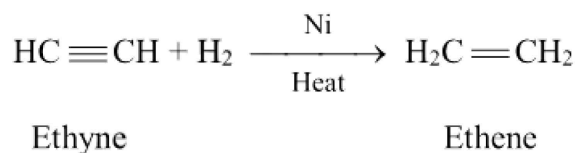
### REACTIONS OF ALKYNES

#### (a) Addition Reaction:

Alkynes undergo addition reaction like alkenes but add two molecules of the reagent instead of one.

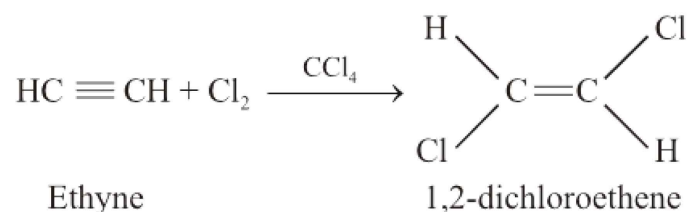
##### (1) Addition of Hydrogen:

Alkynes react with hydrogen gas in the presence of a suitable catalysts like finely divided Ni, Pt or Pd. Initially alkenes are formed which then take up another molecule of hydrogen to form an alkane.

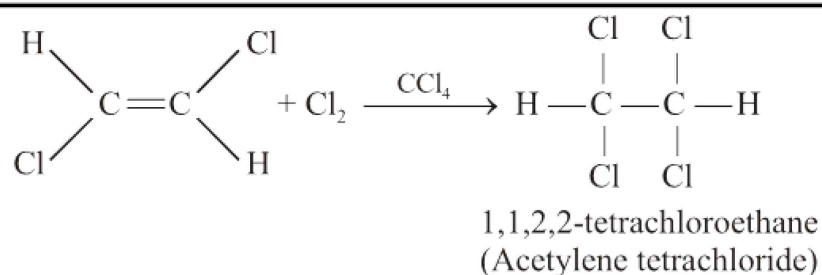


##### (2) Addition of Halogens:

One or two molecules of halogens can be added to alkynes giving dihalides and tetra halides respectively. Chlorine and bromine add readily while iodine reacts rather slowly.

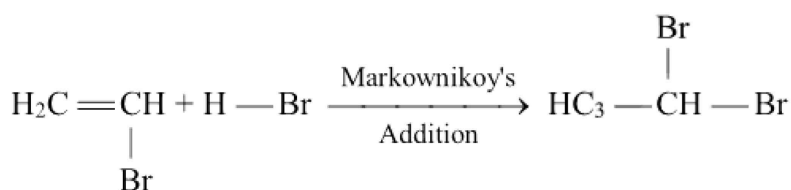
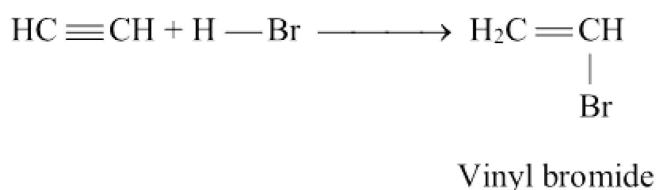






### (3) Addition of Halogen Acids:

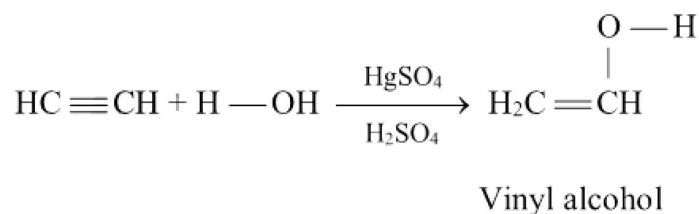
Alkynes react with HCl or HBr to form dihaloalkanes. Addition of second molecule in vinyl bromide takes place according to Markonikov's rule.



1,1-Dibromoethane (Ethylidene bromide is geminal dihalide)

### (4) Addition of Water:

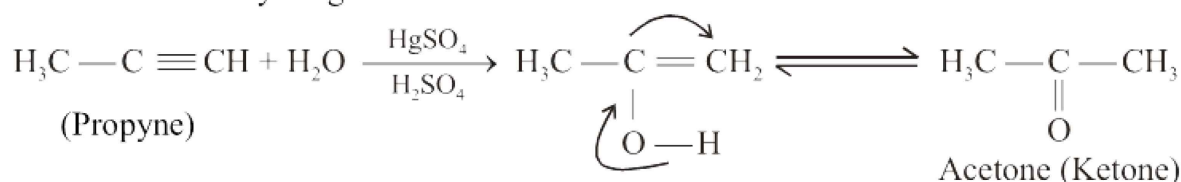
Water adds to acetylene in the presence of mercuric sulphate dissolved in sulphuric acid at 75°C. The reaction is important industrially.



Vinyl alcohol is an unstable enol. The enol has the hydroxy group attached to a double bonded carbon atom and isomerises to acetaldehyde.

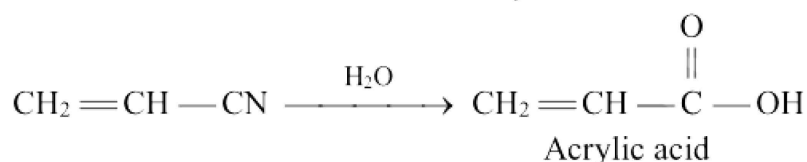
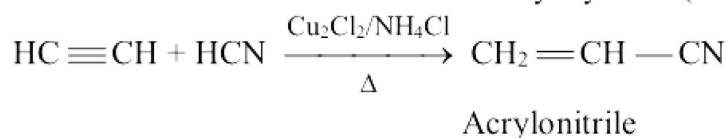
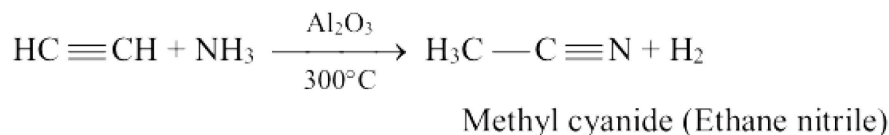


All other alkynes give ketones.



**(5) Addition of Ammonia and Hydrogen Cyanide:**

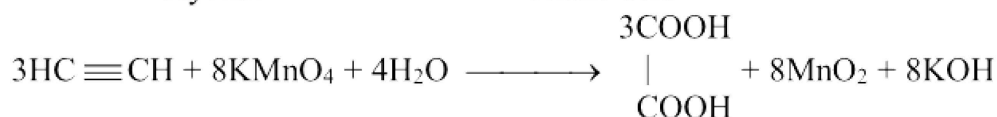
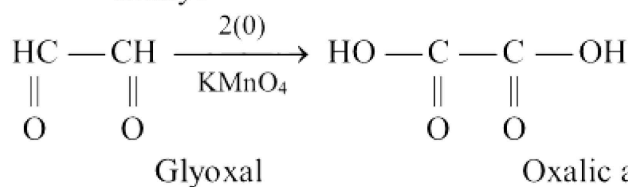
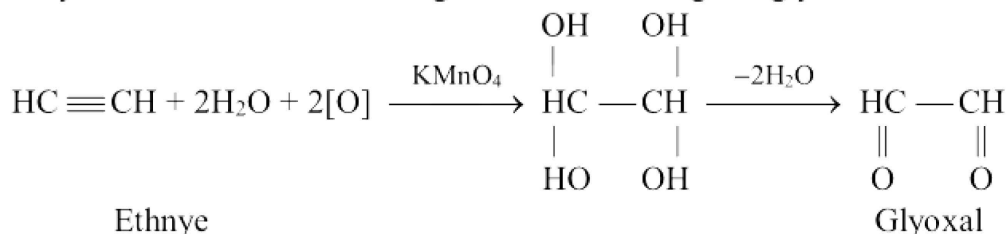
Addition of  $\text{NH}_3$  and  $\text{HCN}$  to ethyne in the presence of suitable catalysts, give nitriles.



Acrylic acid is used in weather resistant paint.

**(b) Oxidation Reactions:**

**(1)** Ethyne on oxidation with strong alkaline  $\text{KMnO}_4$  gives glyoxal.



**(2) Combustion:**

Ethyne when burnt in air or oxygen, produces heat and evolves  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The reaction is highly exothermic and the resulting oxyacetylene flame is used for welding and cutting of metals.

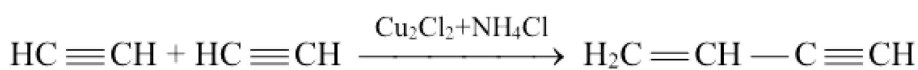


**(c) Polymerization:**

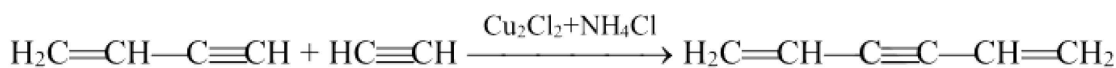
Alkynes polymerize to give linear or cyclic compounds depending upon the temperature and catalyst used. However, these polymers are different from the polymers of the alkenes as they are usually low molecular weight polymers.

**(1) Acetylene to Divinyl Acetylene:**

When acetylene is passed through an acidic solution of cuprous chloride and ammonium chloride and allowed to stand for several hours at room temperature, vinyl acetylene and divinyl acetylene are obtained.

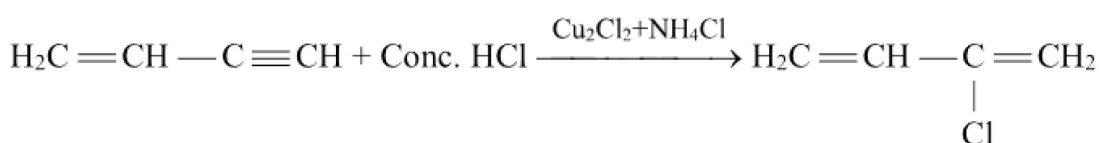


Vinyl acetylene (But-1-en-3-yne)

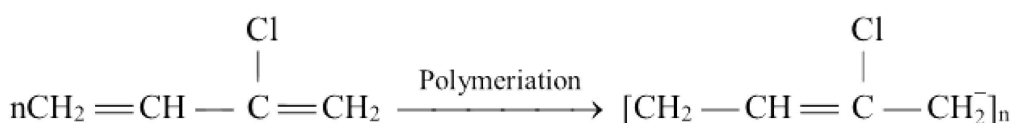
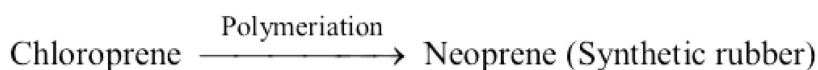


Divinyl acetylene  
(Hexa-1,5-dien-3-yne)

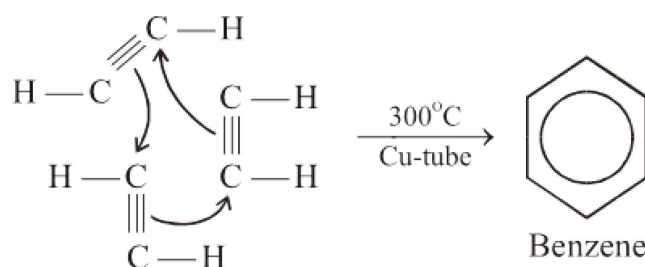
If HCl is added to vinyl acetylene, chloroprene is obtained which readily polymerize to neoprene, used as synthetic rubber.



(Chloroprene)

**(2) Acetylene to Benzene:**

When acetylene is passed through a copper tube at 300°C, it polymerizes to benzene.



## ACIDIC NATURE OF ALKYNES

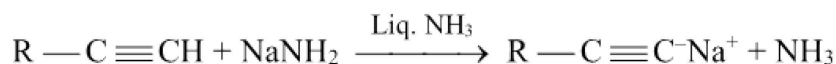
Alkynes differ from alkenes and alkanes. They have acidic hydrogen in them. The hydrogen atom attached to triple bonded carbon atom or sp hybridized carbon atom is acidic in nature.

In alkynes s-orbital of hydrogen is overlapped with sp-hybrid orbital of carbon which has 50% s characters. sp<sup>2</sup>-hybrid orbital has 33% s and sp<sup>3</sup> hybrid orbital has 25% s characters in it. Due to greater s-characters of hybrid orbital of carbon, it attracts the electrons to itself and behaves as more electronegative than sp<sup>3</sup> or sp<sup>2</sup> carbon atoms. Due to greater attraction of sp carbon, slightly negative charge is present on carbon and slightly positive charge is present on hydrogen.



This acidic hydrogen can be replaced by a metal ion to form salts called alkynides. Acetylene has two acidic hydrogens while 1-alkynes (1-propyne, 1-butyne, etc) have one acidic hydrogen while 2-butyne has no acidic hydrogen in it.

When 1-alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained respectively.



Disodium acetylide

Sodium acetylide is a very valuable reagent for chemical synthesis and is essentially ionic in nature.

Acetylides of copper and silver are obtained by passing acetylene in the ammoniacal solution of cuprous chloride and silver nitrate respectively.

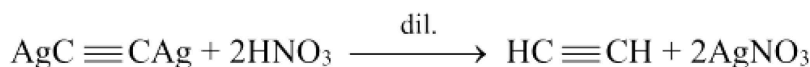
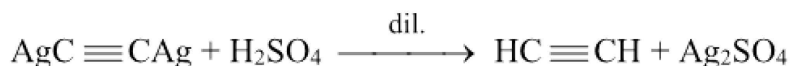


Dicopperacetylide  
(Reddish brown ppt.)



Disilver acetylide  
(White ppt.)

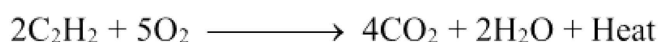
Silver and copper acetylides react with acids to regenerate alkynes.



These alkynides are used for the preparation, purification, separation and identification of alkynes.

### USES OF ETHYNE OR ACETYLENE

- (1) Oxyacetylene flame has temperature about  $3000^\circ\text{C}$  and is used for metals cutting and welding.



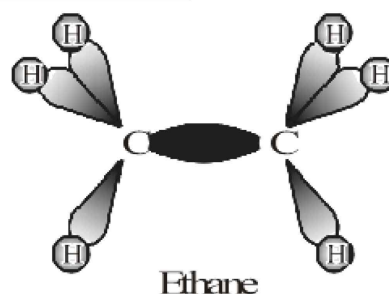
- (2) It is used for the artificial ripening of fruits.
- (3) Acetylene is used for the preparation of alcohols, acetaldehyde and acetic acid.
- (4) It is also used for manufacture of polyvinyl chloride PVC, polyvinyl acetate, polyvinyl ethers, neoprene rubber, orlon and benzene.
- (5) It is used to prepare acetylene tetrachloride  $\text{C}_2\text{H}_2\text{Cl}_4$ , which is a solvent for varnishes, resins and rubbers.

### COMPARISON OF REACTIVITY OF ALKANES ALKENES AND ALKYNES

- (1) Alkanes are the least reactive hydrocarbons. Alkanes have all sigma bonds in them which are strong bonds. In sigma bonds, electrons are very tightly held between the nuclei and makes them stable. A lot of energy is required to break  $\text{C}-\text{C}$  or  $\text{C}-\text{H}$  bond in alkanes.

Electrons of the sigma bonds of alkane are not

attracted by any nucleophile or electrophile. So alkanes do not react with ionic reagents, acids alkalis, oxidizing agent or reducing agents. However, under suitable conditions, alkanes undergo some substitution, combustion and thermal or catalytic reactions. Alkanes do not go addition reactions.

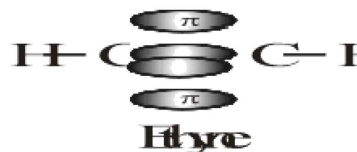


- (3) Alkenes are the most reactive hydrocarbons. Alkenes have one sigma and one  $\pi$ -bond between  $\text{C}-\text{C}$  atoms. Each carbon atom of double bond is  $\text{sp}^2$  hybridized.  $\pi$ -bond in alkene is weak and can easily be broken by any electrophile.



$\pi$ -electrons of alkene are more exposed and can easily be attached by an electrophilic reagent. Alkenes are more reactive than alkane as well as alkynes.

- (4) Alkynes are less reactive than alkenes but more reactive than alkanes. Alkynes have one sigma and two  $\pi$ -bonds between C – C atoms.



The electron density between triple bonded

carbon atoms is very high which draws atoms close together.  $\pi$ -electrons of alkynes are less exposed. Therefore alkynes are less reactive toward electrophilic reagents. Alkynes are however more reactive than alkenes toward nucleophilic reagents.

The decreasing reactivity order of alkanes, alkenes and alkynes is as follows:

Alkenes > Alkynes > Alkanes

### ELECTROPHILES OR ELECTROPHILIC REAGENTS

*“The substances which are deficient of electrons and can accept available electrons from another substance are called electrophiles or electrophilic reagents. (electron – lovings)”. e.g.,*

- (1) **Positive Electrophiles:**

Proton ( $H^+$ ), Chloronium ion ( $Cl^+$ ), Bromonium ions ( $Br^+$ ), Nitronium ion ( $NO_2^+$ ), Nitrosonium ion ( $NO^+$ ), Carbonium ion, ( $CH_2^+$ ,  $RCH_2^+$ ,  $R_2CH^+$  or  $R_3C^+$ ).

- (2) **Neutral Electrophiles:**

O  
||  
AlCl<sub>3</sub>, BF<sub>3</sub>, ZnCl<sub>2</sub>, SO<sub>3</sub>, R — C — Cl carbonyl carbon of aldehyde and ketone

O  
||  
— C —, carbon adjacent of halogen in alkyl halides. ( $CH_3^{\delta+} — Br^{\delta-}$ ).

### NUCLEOPHILES OR NUCLEOPHILIC REAGENTS

*“The substances which donate a pair of electrons to electrophile and form a new covalent bond are called nucleophiles (nucleus – loving)”. e.g.,*

- (1) **Negative Nucleophiles:**

Halides ions ( $Cl^-$ ,  $Br^-$ ,  $I^-$ ), Alkoxy  $R — O^-$  hydroxide ( $OH^-$ ) cyanide, ( $CN^-$ ), Amide ion ( $NH_2^-$ ), Carbanion ( $CH_3^-$ ,  $RCH_2^-$ ,  $R_2CH^-$ ,  $R_3C^-$ ).

- (2) **Neutral Nucleophiles:**

Ammonia  $NH_3$ , Water  $H — O — H$ , Alcohol  $R — OH$ , Alkyl hydrogen sulphide  $R — SH$ . Alkyl amines ( $R_3N$ ,  $R_2NH$  or  $RNH_2$ ).